SYNTHESIS OF PHTHAL-AS-EINS AND SUCCIN-AS-EINS FROM γ - KETO ACIDS AND THEIR STRUCTURAL INVESTIGATIONS WITH SPECIAL REFERENCE TO COLOUR AND CONSTITUTION

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By

Smt. KUSUM LATA SHAKYAWAR
M. Sc, M. Ed.

DEPARTMENT OF CHEMISTRY
DAYANAND VEDIC POSTGRADUATE COLLEGE,
ORAI-285001 U.P.

ORAI
DATED

CERTIFICATE

It is to be certified that the work presented in the thesis entitled, "SYNTHESIS OF PHTHAL-AS-EINS AND SUCCIN-AS-EINS FROM γ - KETO ACIDS AND THEIR STRUCTURAL INVESTIGATIONS WITH SPECIAL REFERENCE TO COLOUR AND CONSTITUTION." has been carried out under my guidance and supervision by Smt. Kusum Lata Shakyawar, M. Sc. himself for the degree of Doctor of Philosophy in Chemistry of Bundelkhand University, Jhansi.

I further certify that the work and the approach adopted by the investigator is entirely original and it has neither been carried out anywhere else in the same form and manner nor it has been submitted for any other degree of this or any other university.

Smt. Kusum Lata Shakyawar has put in more than 200 days of work in the Chemical Laboratory, of Dayanand Vedic College Orai, (U.P.).

31/8/07

(Dr. IM BEG)
HOD & READER
Department of Chemistry
Dayanand Vedic College
Orai 285001 (U.P)

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KSh

ORAI
DATED : 31/8/07

(Smt. Kusum Lata Shakyawar)
M.Sc-M.Ed.

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CHAPTER ONE

INTRODUCTION

CHAPTER I

INTRODUCTION

A.I Beatue du diable of the fascinating variety of things that fulfil our universe may be largely attributed to the most captivating aesthesiogen: the colour. The man, since the advent of civilization, has always enjoyed colour. Captivated most by its fascination, he has ever since tried to duplicate the colours of nature and has exploited them in a number of ways. Ancients used coloured substances of natural origin to decorate their skin, fabrics and other materials. However, the choice was limited. It was only in the nineteenth century that man succeeded in synthesizing the coloring substance in the Chemist's laboratory. Today, the colourants having every colour of the rainbow and their various hues and shades have been synthesized. In many cases, the man has improved over nature and given mankind not only many new substances with colours and shades but also those that are far more superior.

A. 1 DEVELOPMENTS IN THE HISTORY OF COLOURANTS:

Even though its appeal has only been aesthetic, colour has increasingly been called upon to sell products and so vast industries are now dependent upon the availability of artificial colourants. Clothing's, carpets, well paints, plastic veneers, colour photographs, medicine, food and what not, all contain colouring substances. Throughout the history of man, dyes and pigments, both natural and artificial, have been important articles of commerce. Consequently, considerable interest has been shown in the theoretical and empirical evaluation of relationship between their colour and molecular structure. The widening areas into which the colours now intrude have accentuated this interest. In fact, colour – structure relationships are now of value to the scientists working in many seemingly unrelated disciplines. Save apart business and industry, dyes and pigments enjoy their applications in science[2], biology[3], medicine [4-31], engineering, architecture and technolgy[32-34], art.

Philosophyand psychology[35] and above all, moden living as we see every dry day[34] . Liquid crystal systems, high energy radiation sensors and organic dye lasers[36-40] are recent examples of varied uses of synthetic colouring matters. But the burden to meet the ever-increasing demand of artificial colourants consequent upon a bewildering range of their applications rests with the humble organic chemist.

1.2 NATURAL COLOURANTS:

In the ancient times the materials used to produce colours were few in numbers and were obtained from vegetable sources. The three most prized colours were the blue indigo, the red madder and the yellow of the saffron. Other colouring matters were those of animal origin. 'Tyrian Purple' obtained from a small snail 'Murex Bandaris' found near Tyre was so costly that it was available only to those of high status. Henace its name 'Royal Purple'. Then there was 'Cochineal' obtained from the dried body of female insects cacti;. These along with some other natural products constituted the dyeing material of those times.

1.3 SYNTHETIC COLOURANTS :

The properties of natural colournats were far from ideal, and together with their limited availability from sources of supply, encouraged the early search of synthetic dyes with superior properties and availability in plenty. However, only a few additions couldn't made to the existing natural colourants until the rise of the modern synthetic dye industry 41 during the closing years of the nineteenth century.

The modern multi billion dollar synthetic dye-stuff industry owes its initiation to the academic research due to Perkin[42] and the vigorous efforts by such leading organic chemists as Haffmann , Baeyer , Caro , Griess , Graebe , Liebermann , Otto fischer , Emil fischer , Nietzki[43] and a host of others. Later however, research chemists more closely concerned with industry largely carried out the development of new organic dyes some of them are Sandmeyer , Heumann , Schmidt , Green[44] etc.

PICRIC ACID was born to Woulfe in 1771 as the first synthetic dye by the action of nitric acid on natural Indigo. Not until 1885 was a technical method introduced to prepare it from coaltar AURIN, the ROSOLIC ACID, became in 1834 the first coaltar dye reported by Ferdinand Runge. It along with usual mordants produced the red colours and lakes that rivaled those produced from natural dye cohineal and Alizarin. Yet neither of these compounds were being manufactured on a commercial scale. The unreliability of supply and the heavy cost was the cause. That, for the little knowledge about the components of coal tar and that for Kekule's theory of structure of benzene was not proposed until 1865, Ringe's experiments couldn't be extended. As early as 1843, Hoffman had observed that aniline prepared at the time gave red colours under certain conditions. In 1856, Perkin[45] oxidized aniline sulphate with

potassium dichromate and obtained a purple dye called MAUVE. Mauvine or aniline purple was the first dye to be manufactured commercially. It was the sensation of 1862 World Exhibition in London. The first coal tar dye caught on and the race for new dyes and colours began in right earnest. From a waste product the coal tar was transformed into a commodity of immense use. Synthesis of martius yellow, caro's induline blue and Hoffman's violet followed quickly and was accepted widely. The discovery that the colouring matter could be prepared by the oxidation of aniline led to the study of behaviour of this base towards various oxidizing agents. Soon, thereafter, the bright red dye FUCHSIN was prepared in 1859 by Verguin in lyons, france by the oxidation of aniline by tin chloride, which made an even greater impact than the MAUVE. After Hoffman showed that FUCHSIN is a derivative of tri phenylmethane , this class of dyes was investigated extensively and came into widespread use.

The discovery of early synthetic aniline dyes was necessarily the result of intuitive following of clues derived from fortuitous experiments since the constitution of even benzene was unknown. In the year 1865 Kukule published his theory of the structure of benzene and thus paved the way for elucidation of the structure of organic compounds aromatic in nature and for the development of dye industry on a rational basis. The artificial dyes although more brilliant, were less permanent than the natural dye chemists set out to work analyzing the structure of the natural products[46-50].

The structure of Alizarin, the popular red dye from the route of madder, was quickly determined in 1868 by Carl Graebe and Carl Liebermann[51], to be a derivative of anthracene. Benzene, naphthalene and anthracene are colourless products of coal tar distillation. By simple chemical addition of chromophoric groups[52] beautiful dyes can be created. This finding in the 19th century excited the fashion world to colourfull fantasies. Graebe and Liebermann[53] in 1868 afforded the synthesis of alizarin. In 1869, Graebe, Liebermann and Perkin were able to achieve its commercial production. This followed the manufacture of a family of alizarin like dyes with different colours. In 1871, Baeyer prepared FLUORESCEIN and in the same year caro prepared Eosine after the start of commercial production of resorcinol. While the attention of the chemists were directed towards the synthesis of alizarin, another class of dyestuffs, the azo dyestuffs, appeared in the market in 1876. Griess had already synthesized azo compounds in 1862 and one member of group BISMARK BROWN had already been prepared on the commercial scale since 1863. In 1875 Caro discovered CHRYSOIDINE and indicated the technical value of the Griess method of preparing the azo compounds.

When azo dyestuffs were first introduced, it was considered that only orange and yellow colours could be obtained in this series. This idea was dispelled by the discovery of FAST RED A by Caro in 1878.Thus we see that Heinrich Caro[54] contributed much to the synthetic dye industry.

By the turn of the century, in 1879 the oldest known colouring matter indigo was synthesized by Baeyer and was put to commerce in 1880. However, Karl Heumann[55] achieved successful industrial production of synthetic indigo 1890. Baeyers Indigo synthesis marked the begging of the chemical industry and led to the development of organic chemistry whose economic strength was then recognized. Thus was born the chemical industry[56].

Since then the progress in the field of dyes has been very rapid [57-85]. Here is a list of new milestones: Direct dyes from azo compounds for cotton were introduced in 1880; sulpur colour from coal tar derivative in 1893; anthraquinone dyes, vat dyes in 1901; azoic dyes or ice colours in 1911; acetoanilides in 1923; phthalocyanines in 1934; fluorescent brightening agents in 1940 and fiber reactive procion dyes in 1956. Thus natural dyestuffs were almost completely displaced by synthetic colourants. Fundamental research on new dyes is constantly in progress [86-100] and thus synthetic dyes are dominating the field now. Today the industry occupies an important place among the major chemical industries.

A.4 DYESTUFFS AND PIGMENTS : DEFINITION

A dye-stuff is mostly an organic compound, which may be used to impart colour to a substance. It may be used as for the colouring of animal, vegetables or synthetic fibres and similar products such as wool, cotton, silk, linen, rayon, fur, leather, paper, nylon, or other materials such as oils, waxes, rubber and plastic. In these cases, the dyes may form a chemical union with the substance being dyed or it may become associated with it in an intimate physical union. Dyes, which are more or less soluble in water or may be made so simply, by a simple chemical reaction such as reduction, generally are used for dyeing and printing of fibers and related materials. Dyes of solvents, oil, waxes or plastic are either soluble in these media or else so finely divided that may be effectively dispersed throughout to give high colour strength. These insoluble colouring substances are called pigments[101].

1.5 CLASSIFICATION OF DYES:

Fundamentally all the organic dyestuffs are classified in the following two ways:

1. Based on method of application of the dyes.

1. Based on the chemical constitution of the dyes.

The first classification of dyes is very useful to the dyers who are mainly concerned with the process of dyeing. Moreover, this classification gives the various method of dyeing various fibers with different dyes. Thus, the dyes are classified into the following categories:

(i) Acid dyes, (ii) Basic dyes, (iii) Direct dyes, (iv)Mordant dyes, (v) Ingrain dyes, (vi) Vat dyes (vii) Sulphur dyes, (viii) Synthetic fiber dyes and (ix) Other synthetic dyes.

The second classification is mainly useful for those chemists who are mainly interested in chemical constitution of the dyes. O.N.witt[102] was the first who suggested a classification of the dyes according to chromophore or the essential colour producing group present in the dyes. But a number of dyes contain the same chromophoric group and so it became necessary to adopt a classification on the basis of the characteristic structural groups present in the dye molecule. This chemical classification divided all the dyes into the following principal groups put under two main classes: Homocyclic hetro ring absent and Hetrocyclic- atleast one ring present.

(A)Hemocyclic dyes:

(a) Anthraquinone dyes, (b) Azo dyes, (c) Azomethine dyes or benzlidene dyes, (d) Diphenylmethane dyes (e) Ethylenic dyes, (f) Ketoimine dyes, (g) Nitro dyes, (h) Nitroso dyes, (i) Pyarazolone dyes (j) Quinonimine dyes and (k) Triphenylmethane dyes.

(B) HETROCYCLIC DYES:

(l) Acridines, (m) Azine, (n) Azoxy and nitrosostilbene dyes, (o) Flavones, (p) Indigoids, (q) Oxazine dyes, (r) Quinoline dyes: (i) Cyanines (ii) Isocyanines, (iii) Pynacyanols, (iv) Dicyanines, (v) Carbocyanines; (s) Sulphur dyes: (i) Thiazine dyes, (ii) Thiazoles, (iii) Sulphur blacks; (t) Phthalocyanines, (u) Xanthen dyes: (i) Fluorones, (ii) Phthaleins, (iii) Pyronines, (iv) Succineins, (v) Rosamines, and (vi) Rhodamines.

1.6 NOMENCLATURE SYSTEM:

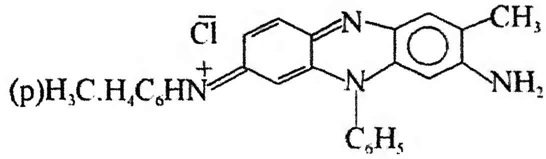
There is no uniformity in naming of the synthetic dyes. In most cases they bear the name given to them by their manufacturers. Furthermore, each dyestuff may have a number of names or different dyes may be known by the same names. In the colour index of the society of Dyers and colourists [103], however each dye is given an individual nuber called the colour index Number abridged as C.I.No.

1.7.PHTHALEINS:

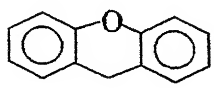
These dyes are the subject of the present work, which were first discovered by Baeyer[104] in 1872 as a new class of dye. He prepared GALIEN, FLUORESCEIN and PHENOLPHTHALEIN by condensing phthalic anhydride with pyrogallol; resorcinol and phenol respectively in the presence of a dehydrating agent like sulphuric acid or zinc chloride. Baeyer established that the parent member of the group phenolphthalein was dihydroxy derivative of phthalophenone which in turn could be degraded to triphenylmethane. Thus, he illustrated that phenolphthalein was a derivative of triphenylmethane. Following analogous arguments[105] for fluorescein and for similar dyes called rhodamines; Baeyer classed them under triphenylmethane dyes which some authors[106] still follow. Elsewhere[107] only phenolphthalein, its tetralodo derivative and sulphophthaleins constitute the group, phthaleins and fluorescein its derivative uranine, eosine, mercurochrome, and rhodamines constitute another group called xanthenes. Both phthaleins and xanthenes, in turn, form a subclass of triphenylmethane dyes.

In Baeyer's accord, all the dyes prepared by the condensation of phthalic anhydride with different phenols, aromatic hydroxyl compounds are grouped as phthaeins. Pyronines, rhodamines, and other similar dyes, which could be prepared in a similar manner that used for the preparation of phthaleins, phthaleins included, contain a Characteristic dibenzo-1,4 pyran nucleus dibenzo-1,4-pyran is called xathen[108] which is an inner anhydride of o-o' dihydroxydiphenylmethane. From xanthenes these dyes can be derived by introducing auxochromes[109] into position-3 and-6, i.e. in para position with respect to carbon atom linking the two benzene rings. Therefore, in the classification used herein these dyes are grouped as xanthen dyes or xanthens[110].

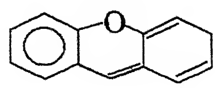
In facts phenolphthaleins, although a phthalein, is not a xanthene dervative[111]. yet generally, xanthenes are prepared[112] like phenolphthaleins by the method mentioned earlier.



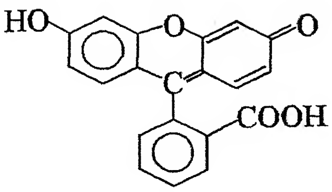
MAUVEIN



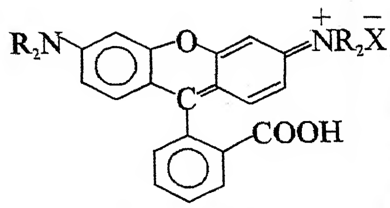
XANTHEN



3H-ISOXATEN

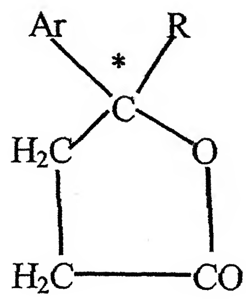


FLUORESCEIN
QUINONOID FORM



RHODAMINES

Succineins were prepared by the condensation of aromatic hydroxyl compounds with succinic anhydride in presence of concentrated sulhuric acid as the dehydrating agent and are represented as follows:



Succineins

B. COLOUR AND CONSTITUTION OF ORGANIC MOLECULES:

The most common manner in which the colour is generated is by the absorption of certain wavelengths of the visible light. Organic compounds with extensive conjuction absorb certain wavelengths of light because of $\pi-\pi^*$ and n---- π^* transitions. We do not observe the colour absorbed but we see its complement that is reflected. A complementary colour sometimes called a subtraction colour is thus the result of the subtraction of some of the visible wavelengths from the entire visual spectrum.

Before the theories of electronic transition were developed, it was observed that some types of organic structures gives rise to colour while other don't the partial structures that are necessary for colour, the unsaturated groups[115] can undergo $\pi-\pi^*$ transition, were called chromophores, a term Witt[114] coined in 1876 (Greek chroma-colour and phorous-bearing). These he specified as nitro, nitroso, azo and carbonyl groups that he suggested fall in this category. Molecules cantaining such groups e.g. nitrobenzene and azobenzene were referred to as chromogens since they had potentiality for developing colours even if they were not in themselves intensely of colours. Witt observed that presence of some other groups caused an intensification coloured. These groups were called auxochromes (Greek auxanein-to increase). These groups which were called the typically polar such as hydroxyl – or amino - did not in themselves produce colours, as we knonow that they can not under go $\pi-\pi^*$ transitions, but could produce hypsochromic effect i.e. a shift in the absorption bands to shorter wave lengths, or a bathochromic effect where the shift is in the opposite direction, i.e. to longer wave lengths, as they can under go transition of n electrons. However, in practice, intense colour can be obtained without the presence of auxochromic groups and it has since been shown that this concept has nothing of scientific significance. The theories of Graebe, Leibermann, Witt, Neitzki[115] Armstrong[116] etc, were the results of successful attempts to determine the molecular structure of organic compounds and interpretation of colours in terms of chemical structure without regard to its physical causation. During the early years chemists were intrigued by the elusive relationship between the absorption spectra and the molecular structure and therefore the progress was severely hampered for want of suitable theory for the light absorption precess itself. Today, thanks to the advent of quantum theory, we are in a more fortunate position, and mathematical treatments of varying lavels of sophistication are available for the prediction of absorption spectra. Equally important are the qualitative treatments of light absorption, which have stmmed from the valence bond the molecular orbital theories and which can be used to predict qualitatively the effects of structural changes on the absorption spectra of a molecule.

B. 1 THE MECHANISM OF ABSORPTION OF LIGHT BY MOLECULES

A complete and satisfactory explanation of the colour of the organic compounds was found to be associated with absorption and transmission of light in general with the spectra of the molecule. The absorption of light was recognized to be associated with certain process of molecule energy changes and the process could also take place with many other substances besides those as appeared coloured to the human eyes. The colour as it appears to the human eyes is only a special case of the general feature of general phenomenon of absorption of electromagnetic waves and the colour of the substance for which the human eye is sensitive is determined by the selected absorption of light consisting of those waves. The phenomenon of light absorption is not limited to the visible part of the spectrum only but takes place in the ultra and infra red regions as well, as said befor. Since white light imparts different colours to defferent chemical compounds, it is obvious that colour is a function of the chemical constitution of the molecules.

The wave particle duality of matter when applied to the electromagnetic radiation and to atomic particle forms the basis of quantum theory that uses the famous de Broglie relation

$$P=h/\lambda \qquad \text{................Eq. 1}$$

Where p is the momentum of the particle, λ is its associated wavelength and h is the Planck's constant.

The absorption and emission of light by matter[117] is explained by the wave properties of light. An electromagnetic wave is characterized by an electric vector E and a magnetic vector H which form a mutually perpendicular set of axes with the propagation of the vector C. The absorption of light arises mainly through an interaction of electric vector of light with the electrons and nuclei in the molecule. The magnetic vector is only important for an understanding of phrnomenon of optical rotaion. A molecule initially in a state of E_a can absorb light of frequency v, provided there is existing a state E_b by an amount E that satisfies the relation.

$$E = E_b - E_a = h\nu = hc/\lambda \text{ .... Eq. 2}$$

And it is said that the molecule has absorbed a photon of energy hv and is in the excited state E_b. The stability in the excited state is limited and after a very short time e.g. less than 10^8 second the excited molecule dissipates its excitation energy and comes back to the ground state E_a.

A molecule can exist in many excited states corresponding to the changes in its rotational, vibrational and electronic energy lavels. And all these energies are quantized. Therefore, the absorption spectra can be further classified[118] into three types:

1. Pure rotation spectrum which is associated with the changes in the rotational states of the molecule without the simultaneous changes in the vibrational and the electronic states. Since the separation between the various rotational levels are relatively small, it follows from Equation 2 that the corresponding occur in the far infra red and the microwave regions.

2. Rotational – vibrational spectrum is associated with transitions in which the rotational and the vibrational states of the molecule are altered, but the electronic state remains unchanged. The energy differences are relatively greater than in pure rotational spectrum and, accordingly, the absorption occurs at sjortre wavelengths i.e. in the near Ingra red region.

3. Electronic spectrum that arises from the transitions between the electronic states, changes both the vibrational and the rotational levels. Therefore, a broad-spectrum band instead of a sharp line is observed. Relatively large differences are involved in the electronic spectra, which occur at still shorter wavelengths, i.e. in the ultra violet and the visible region.

Since the electrons can only be raised upto certain levels. ΔE must have some definite value; i.e. absorption of light by a molecule is not indiscriminate and discontinuous, but slective and gives rise to colour. A part from the frequency of the absorption band, colour also depends upon the intensity of the absorption that in turn depends upon probability of transition between the two energy levels concerned. The probability of the photon being absorbed depends upon the magnitude of the transition dipole moment between the two concerned energy states. The light absorption by a molecule[119] can only occur when dipole moment changes in a molecule. The more symmetrical the molecule, smaller is the probability of the transition dipole and, therefore, the less likelihood of absorption of light by the molecule. Calculations have shown that greater is the transition dipole, greater is the intensity of absorption. The introduction of a group in a molecule that decreases the symmetry will thus increase the transition dipole and consequently increase the intensity of absorption. At same time, however, new ‘resonance paths’ may be introduced, and hence, not only a change in the intensity of absorption occurs, but also there is shift of the band to longer wave legths.

B.2 THEORETICAL MODELS FOR CALCULATING LIGHT ABSORPTIONS :

The process of absorption of ultra violet and visible light by a molecule, as already mentioned, causes an electronic from a lower to a higher energy level; or more exactly causes an excitation from the highest energy level in the ground state to the lowest permitted energy level in the excited state as shown in figure to follow.

Compounds where the valence electrons are involved in sigma bond formation such as saturated hydrocarbons, only show absorption due to excitation of an electron a σ^* antibonding or a higher orbital. The energy requirement are high, above 150 kcal $mole^{-1}$ and absorption occurs below $2000A^0$ or 200 nm. This type of excitation process is referred to σ-------- σ^* transition, where the asterisk denotes an excited state. In compounds containing lone pair electrons; O,N, S which are not utilized in bonding, the energy requirements for excitations are less since these electrons are generally less strongly held. The n.... π^* transitions (following the nomenclature of Kasha[120]) in simple molecule thus gives rise to spectral bands at the longer wavelengths than those associated with σ------σ^* or π------π^* transitions. Proton addition to the non-bonding electron pair in O, N, or S atoms causes the disappearance of the band at long wavelengths confirming that these non-bonding electrons take part in the excitation process. π------π^* transitions occur in the molecules containing double bonds in which there is an overlap of p-orbital causing formation of π-bonds. Because the overlap of p-orbital is not as great as in σ- bonding π------π^* transitions generally occur at the wavelength intermediate between those σ----σ^* and n----π^* transitions, i.e. in the near ultra violet and the visible region of the spectrum.

Thus, form the foregoing discussion, it becomes clear that to understand the colour of a compound, it is necessary to have a knowledge of the electronic structure of the molecule and its effect on the absorption of light in the visible and the near ultra violet region of the spectrum. For this purpose, three main theoretical approaches to the problem have been made.

B.3 MOLECUAR ORBITAL THEORY (MO) THEORY :

It is necessary to explain the term antibonding, which arises from the concept of the molecular orbital theory. It is best illustrated in the case of hydrogen molecule. When the constituent atom A and B are at equilibrium distance characteristic of the stable molecule, the two atomic orbitals ϕ_A

and ϕ_B, each of which accommodates one electron, will combine to form two molecular orbitals. The first of the lowest energy, is represented by the wave function ψ_B and is called the bonding orbital. This orbital has characteristics separately possessed by ϕ_A and ϕ_B and may be written in a simplified treatment as a linear combination of the two,

$$\psi_B = \phi_A + \phi_B$$

Since molecular orbits arise from the atomic orbitals without the consideration of the electrons they have to accommodate. This treatment is referred to as Linear combination of Atomic Orbitals. The second molecular orbital ψ_A is formed in hydrogen with the condition that.

$$\psi_A = \phi_A - \phi_B$$

This ψ_A is the antibonding molecular orbital. The electron density or probability of finding an electron at a given point in this system is given by ψ^2.

The charge distribution in both molecular orbitals is cylindrically symmetrical. In the bonding orbital, the electron density is greatest between the two nuclei. In the antibonding orbital it is low between the two nuclei and the more stable configuration of the molecule is when the two nuclei are farther apart. It is this energy difference between the two molecular orbitals, which determines wavelength of the absorbed or the emitted light.

The energies of ψ_A and ψ_B molecular orbitals may be represented by the combined energy level diagram drawn on a following page wherein the electrons, x, contributing to separate functions ϕ_A and ϕ_B are shown combined in the case is zero. The two molecular orbitals ψ_A and ψ_B lie at equal difference in energy above and below the individual atomic orbitals. When the degree of interaction or overlap is positive, it can be shown that the antibonding orbital is displaced to higher energy above initial energy and the bonding orbital is displaced to a lower energy to the same extent. Dewar[121] has extended this method of energy demonstration to hybrids of classical structures i.e. where the wave functions ϕ_A and ϕ_B differ in energy, using as an example two classical structures of Michler's Hydrol Blue. The interaction of the two classical structures will give rise to two hybrid states, one of higher energy and the other of lower energy. The energy difference will be smaller when the energies of classical structures

are comparable i.e. mesomeric; and the absorptions occurs at longer wavelengths than when the classical structures have greater divergence in energy.

In the ground state of hydrogen, according to Pauli's Exclusion Principle, the electrons have opposing spins and the state in known as singlet state. Both electrons occupy ψ_B bonding molecular orbital. In the first excited state, one electron is transported to an antibonding orbital. Since the electrons are now in different orbitals, the exclusion principle is no longer applicable and the electrons may now either be paired to give an excited singlet state, or unpaired to give a triplet state. In the latter case, there are three possible states all having the same energy since the z-components of the spin quantum numbers of the two electrons may be both +1/2 or both-1/2 or one may be +1/2 while the other is -1/2. The z-component of the resultant angular momentum may thus be 1, 0, or -1 and the three possible states are known jointly as the triplet state. A further excited state is possible when both the electrons occupy the antibonding orbital. Since the exclusion principle is now applicable, this must be, of necessity, a singlet state, the excited singlet state.

This elementary MO treatment can be extended to molecules which are electronically more complex, such as nitrogen and carbon monoxide, but which, as molecules, are relatively simple, provided due account is taken of hybridization in the simplifications and assumptions have to be made. In applying the theory it is necessary to neglect all over lap integrals between non-adjacent to average electron repulsions and to assume they are unchanged by the excitation process.

Further according to the theory of molecular orcitals[123-124] the absorption of the u.v. and the visible light corresponding to the electron cloud of a molecule, resulting in the formation of electronically excited state. According to quantum theory, a molecule can exist only in a limited number of discrete energy states. The electronic structure of a molecule can be built up by the feeding of electros one after another in the lowest available quantum state in accordance with the Aufbau Principle. A concept of united atom i.e. an atom whose atomic number is equal to the sum of the two separated atoms is helpful to understand the filling of electrons in the MO. The electrons, which in the united atom occupy in the excited state, are the antibonding electrons and those and that do not are bonding electrons. The electrons in the atoms that remain unaffected by the process of molecule formation are said to be nonbonding electrons.

It is possible to consider the phenomenon of light absorption from the point of view of the molecular orbital theory. A molecule is excited when one electron is transferred from an orbital of lower energy to one of higher energy. Such transitions can occur only between permitted orbitals. In a molecule a g state go to a u state, or vice vers; transitions $u \rightarrow u^*$ and $g \rightarrow g^*$ are forbidden. Here u and g bear their usual meaning.

The ethylene molecule in its ground state has, in addition to σ-bond, at π - bond i.e a π_g orbital (bonding molecular orbital) in which there is the first excited state π_u orbital (antibonding molecular orbital). If one electron is excited from π_g to π_u a large amount of energy is required and the molecule therefore absorbs in the u.v region in compounds containing more than one double bond and that too in conjugation, delocalization of bond takes place and the molecular orbital formed covers all the carbon atoms of the conjugated system. The electron, therefore, has greater freedom of movement than in localized bonds and the total energy of the system is lowered which decreases the energy difference, ΔE between the highest occupied and the unoccupied orbitals. Thus, as the conjugated extends, the absorption of light takes place at yet longer wavelengths.

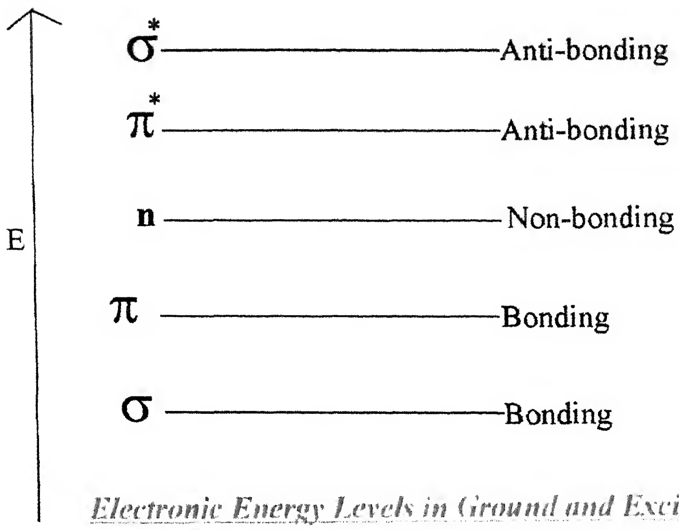
Benzene molecule is symmetrical with all the carbon atoms have equal charges of unity and hence there is no transition dipole in the benzene molecule. It is not expected to absorb the light hence it is colourless. However, a weak absorption in the u.v region is expected and so exhibited. Nitrobenzene is not symmetrical and has unequally charged carbon atoms. Unequal charge produces a definite dipole moment in the molecule of nitrobenzene. The result is high transition dipole and absorption at longer wavelengths.

Furthermore, since nitrobenzene has an extended conjugation, the energy difference between the highest occupied orbitals is decreased, and therefore, it absorbs at longer wavelengths than benzene.

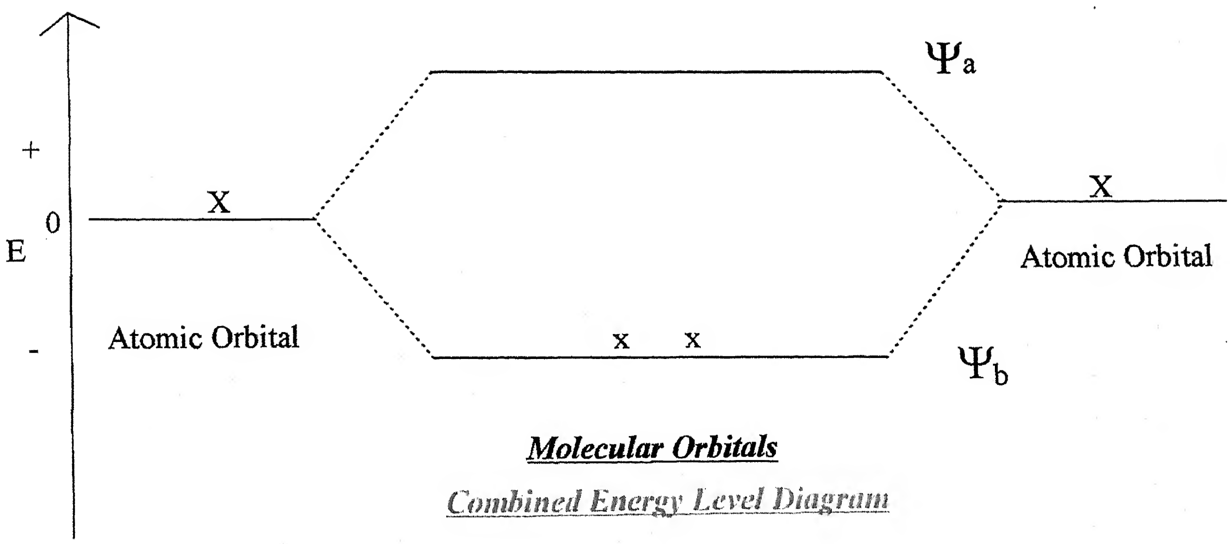
Nitroaniline (orange red) having more extended conjugation and greater separation of charge absorbs light at still longer wavelengths than nitrobenzene. Thus, in general, any such group, which exists in conjugation with benzene ring, happens to pratically cause the shifts in the frequencies of the absorbed light towards the lower region or the wavelengths towards the longer regions. This effect of shifting of absorbed light towards the longer region in the electromagnetic spectrum, is that

which we understand and name as the Red Shift or the Bathochromic shift, or the Bathochromic effect. These shifts, if effects in the derections exactly opposite to those mentioned before, are said to be the Blue shift, or the Hypsochromic shift or the Hypsochromic effect.

Despite the fact that the molecular orbital method appears to be more promising from a quantitative point of view, and it has been possible to calculate the light absorption of many molecules by the ingenious applications of the great Molecular Orbital Method resulting in good agreement that has been obtained between the calculated and the observed values[125] the Valence bond method as applied to absorption of light and prediction of colour stands satisfactory for qualitative purposes; and, therefore, one can not do well in keeping away from it. Thus, the valence bond approach is being discussed in the following section.

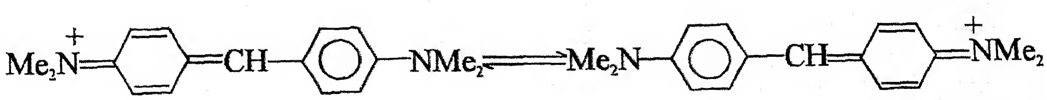


Electronic Energy Levels in Ground and Excited State



Molecular Orbitals

Combined Energy Level Diagram



Classical Structures of Michlers Hydrol Blue

structures lowers the energies of both the ground and the excited states and since charged structures contribute more to the excited state than the ground state, the lowering of the energy will be more prominent in the former than the latter. Thus, a greater resonance among the various charged forms results in the deepening of colour.

It can be safely inferred from the foregoing discussion that a given chromophore will not necessarily give absorption bands in the same position of the spectrum; the rest of the molecule also affects it. Benzene has a definite u.v absorption, 255 nm, ethylene has 185 nm and allylbenzene 249 nm, which is equivalent to the superimposition of spectra of benzene and ethylene. However, styrene has a quite different spectrum, 282 nm where the fine structure of benzene is absent.

Therefore, it can be observed that in styrene, the benzene nucleus is not in the same state, as it was in allylbenzene itself. This observation can be explained by assuming styrene to be a resonance hybried of the structure II, III and IV.

The cyanine dyes, studied by Brooker and coworkers[133] are intensely coloured substances exhibiting a high degree of resonance. These dyes can be represented by the general structures V and VI.

If aromatic ring systems are made part of conjugated chain of a cyanine, the characteristic properties of the chromophore are not altered. Thus, they will still be isoconjugate with an alternate add hydrocarbon anion, and will absorb at long wavelength by virtue of the presence of a nonbonding molecular orbital. The di- and tri-aryl methane dyes are example of this type.

Michler's hydrol Blue. A diaryl methane dye, which is a resonance hybrid of two equivalent structures VII and VIII, absorbs at 607.5 nm in 98% acetic acid. The auramine IX, an impotant commercial dye of diaryl methane series, which is formed by the attachment of an amino group to the central carbon atom of Michler's Hydrol Blue, shows large hypsochromic shift that result from the strongly electron donating amino group and absorbs at 434 nm in ethanol. Substituents other than amino group exert a hypsochromic shift related to electron donating capacity e.g. the attachment of a weaker ethoxy group to the central atom of Michler's Hydrol Blue gives a smaller shift, and the dye is purple, λ_{max} 525 nm.

The triaryl methane dyes, on the other hand, can be divided into two distinct types; those with two terminal amino groups, e.g Malachite Green,

X, and those with three terminal amino groups e.g. Crystal Violet, XI. From the foregoing discussion it is expected that increased number of resonance forms would deepon the colour. But the case of Malachite Green and Crystal Violet proves contrary to the expectations as the colour of the former is deeper than the latter. Malachite Green has two resonating forms where as crystal violet has three. The former shows two absorption bands; one at longer wavelength $\lambda_{max.}$ 621 nm in 98% acetic acid, as expected for the attachment of the neutral conjugating group at any position in the chromophore; and a second band at a shorter wavelength, λ_{max} 427 nm, as this provides a yellow component to the colour, the dye is green rather than blue. Polarization studies have shown that the two transitions are polarized along mutually perpendicular axes[134] . The longer wavelength band is due to polarization along X-axis and the shorter along Y-axis.

Now consider hypsochromic shift shown by Crystal Violet when a dimethyl amino group is substituted in Malachite green. As per resonance theory, Crystal violet ion has a high symmetry and consequently a number of levels will have the same energy although the total number of levels has actually increased and are responsible for the remarkable hypsochromic effect. The average separation of the oscillating charges is, however, increased. Thus, the band is displaced to the shorter region, while intensity has increased due to increased transition probability proportionate to increased number of corresponding levels. Lewis and Calvin proposed that the oscillation of a charge along one direction only is responsible for colour. In Malachite Green all charge is linear oscillations while in crystal violet positive charge can oscillate linearly, horizontally as well as perpendicularly, vertically. Thus 2/3 positive charge is effectively oscillating horizontally in crystal violet. Hence, Malachite Green has a deeper colour than crystal Violet.

B.5 FREE ELECTRON MOLECULAR ORBITAL (FEMO) THEORY :

The applications of MO and VB to theories to dyes practical importance and interest which have complicated structures and their colour is strongly affected by even a slight structural change, requires uthless simplification to obtain even the most general agreement with the observed facts. A third theoretical treatment which on the one hand is highly simplified, and still based on highly valued quantum mechanical treatment on the other, and also avoids rigorous mathematical dilmemma; which has been applied to such complex chromophores with a great degree of success is the one known as Free Electron Gas Method, Free method[137] . This was first proposed by sommerfield[138] , to describe the metallic state and later

extended to organic molecules by Bayyliss[139], Simpson[140,] and notably developed by Kuhn[141-142] and Platt[143.] In its application, this model is limited to consideration of conjugated π-electron systems; but then dyes are considered to owe their colour to these electrons, this theory will be treated in greater detail.

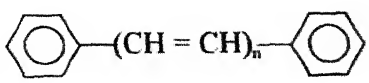
Simplest of all the molecular orbitals methods for conjugated organic molecules, as this theory is, remarkably successful too in calculating transition energies in certain cases. Quite like valence bond and the molecular orbital treatments, in this model too, all the carbon atoms and all the hydrogen atoms are supposed to lie in one plane so that all atomic orbitals are of either σ or π type. The fundamental assumption, rather approximation, in this treatment is the sigma-pi-separation principle[144] , i.e. the sigma and pi electrons can be treated separately and independently. Consequent upon this specifically characteristic assumed feature of this treatment, and that the pi electrons are comparatively free to move within the conjugated system and, provided that this movement is only in the direction of the conjugated chain, their behaviour can be represented by that of an electron in a box or a potential well. Figure XII represents the potential energy of such an electron, where the minus occurs at the positions of the individual carbon atoms along the chain. The energy shown in the lower part of the said figure represents an assumed constant potential along the chain length. The terminal potential barriers are situated at an arbitrary distance beyond the extreme carbon atoms. The quantum mechanical solution of a wave equation for a particle moving under these conditions is,

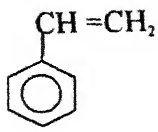
$$\psi_n = \{2/L\}^{1/2} . \sin\{[\pi n/L].x\}^{1/2}$$

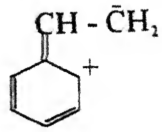
where $0<x<L$, L is the wavelength, x is the distance along the well and n is a quantum number (1, 2, 3, 4......etc) for each value of ψ_n there is a corresponding energy,

$E_n = n^2h^2/8ml^2$ Equation.1

Where h is planck's constant and m is the mass of an electron. In a system consisting of alternate double and single bonded carbon atoms, each carbon atom contributes one pi electron. If the total number of pi electrons is N, then in the ground state are the N/2 levels of the lowest energy since each level is doubly occupied by the electrons having opposing spins =1/2, -1/2 according to Puali's exclusion principle. As no limitation is placed on the number of the possible levels, all others except filled N/2 levels will be

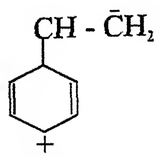






I II III

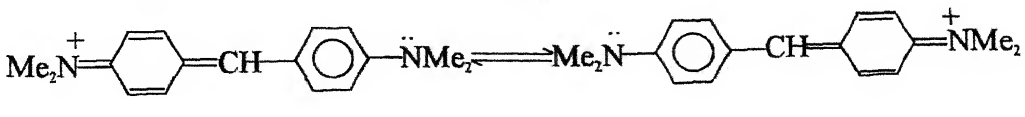
N	0	1	2	3	4	5	6	7
λmax	2515	3190	3520	3770	4040	4240	4450	4650



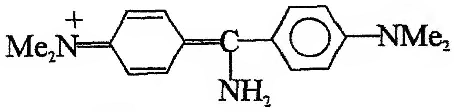
IV

$$R_2N\text{-}(CH{=}CH)_n\text{-}CH{=}\overset{+}{N}R_2 \longleftrightarrow R_2\overset{+}{N}{=}CH\text{-}(CH{=}CH)_n\text{-}NR_2$$

V VI

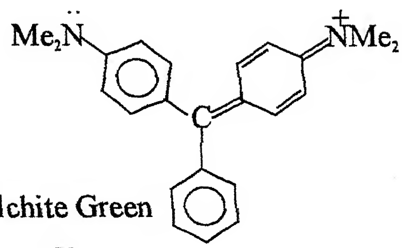


VII VIII



Auramine

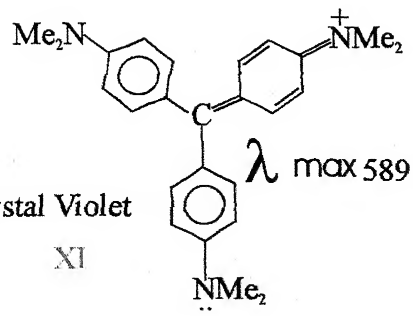
IX



Malchite Green

X

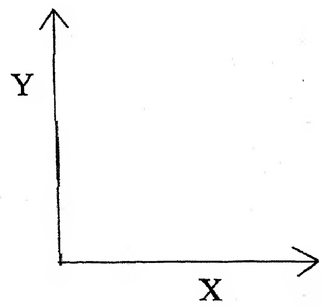
λmax 621 nm in acetic acid

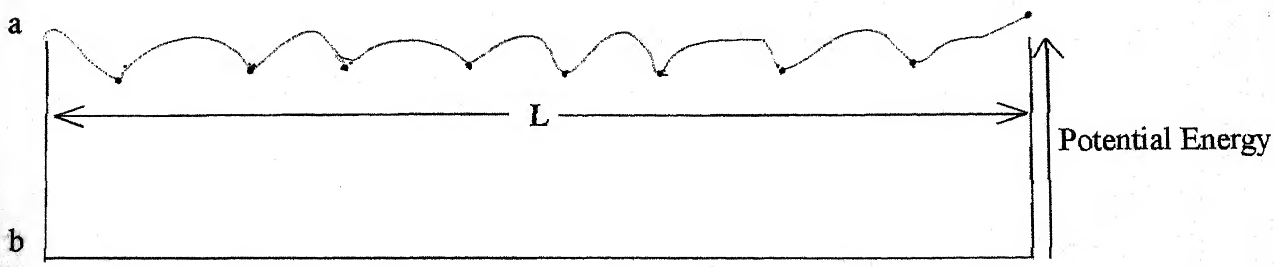


λ max 589 nm (in acetic acid

Crystal Violet

XI





Distance, x . Atoms

Potential Well Diagram XII

empty. When the molecule or the ion absorbs light, this corresponds to one electron jump from the highest filled level with quantum number $n_1 = N/2$ to the next higher energy level, i.e. the lowest empty level with quantum number $n_2 = N/2 + 1$. The energy change or the excitation energy for this transition is therefore,

$$E = E_{N/2+1} - E_{N/2} = (N+1)h^2/8mL^2 \qquad E.2$$

Since $\Delta E = h\nu = hc/\lambda$, where c is the velocity of light and λ is the wavelength in centimeters,

$$\lambda = 8mcL^2 / h(N+1) \qquad E.....3$$

This equation can therefore be applied to any linear conjugated system provided that the number of the double bonds is known and assignment of L is made. Since λ is proportional to L^2, correct values for L are impotent. If need be the above treatment may be extended to three dimensions by supposing the electron to be residing in a three dimensional box.

B.6 APPLICATION OF THE FREE ELECTRON MODEL TO BUTADIENE:

The pi electron structure of 1, 3- butadiene is obtained by assigning two electrons of opposing spins to the lowest orbital and two similarly spin paired electrons to the second lowest. The absorption of light is then assumed to involve the promotion of one of these four electrons to any of the higher orbitals. Equation 3 can then be used to calculate transition energies. The only uncertain parameter is L, the length of the conjugated chain, say that of the potential well. It is usual to regard L as equal to the length of the conjugated chain molecule assuming that the molecule is distorted into a straight line plus one additional bond length at each end of the molecule. For example, 1,3- butadiene has an average bond length of 1.4 A, which gives a value of 7 A, for L. Using aforesaid equation for 1,3 – butadiene a first transition energy of about $3.0\times10^4 cm^{-1}$, or a wavelength of 325 nm is found. The experimental value, 220 nm, may seem indicative of poor agreement but in view of the many gross approximations inherent in the FEM treatment, and its greater simplicity of approach, the agreement is supposed to be remarkably good.

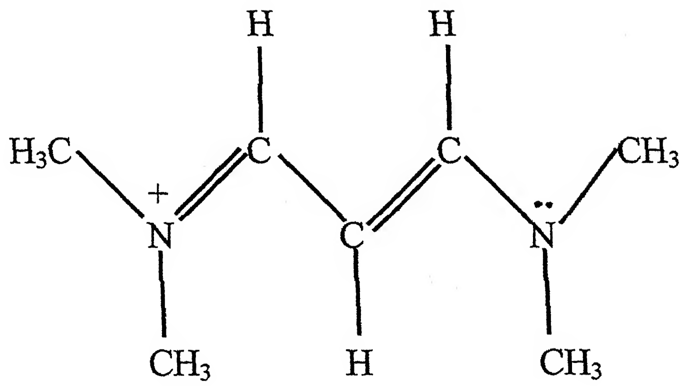
B.7 APPLICATION OF FREE ELECTRON MODEL CYANINES, AZACYANINES, AND BASIC DYES :

The series of compounds known as cyanines typified by figure XIIIa and XIIIb are ideally suited for this method, since they show appreciable bond uniformity that arises from resonance.

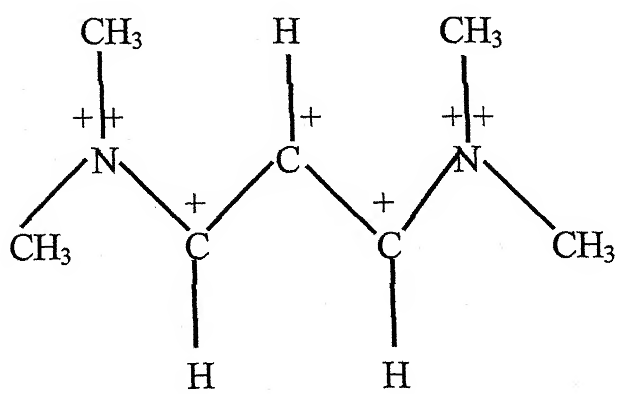
$$Me_2N - (CH = CH)_m - CH = N^+ Me_2 \longleftrightarrow Me_2N^+{=}CH\text{-}(CH = CH)_m\text{-}NMe_2$$

XIII(a) XIII(b)

A symmetrical cyanine dye molecule such as Figure XIVa and b may be considered here in order to find a plausible explanation for its electronic absorption band in the visible region, here the C, N, and hydrogen atoms are linked by sigma bonds and are located in a common plane,



XIV (a) Cyanine molecule



XIV (b) Cyanine sigma skeleton in common plane

Each carbon atom and each nitrogen atom uses its three valence electrons to form the sigma bonds; pi electronic system in each molecule is formed by the contribution of the fourth valence shell electron of each carbon atom and the remaining electrons of the two terminal of nitrogen. These electrons are placed in the electrostatic field of the molecular skeleton. They will be attracted to positive charges of C and N atoms, but their wave function must not have a node at all points of the plane of the molecule. They form an electron gas, which in the shape of a charge cloud stretches along the cyanine chain, both above and below the plane of the molecule. N has five electrons and in the said cyanine dye, three are used form sigma bonds, thus N atom with no charge sign contributes two electrons to the pi electron gas and that we find a total of six pi electrons or three pi electron pairs in this case. Now a single pi electron is considered in the electrostatic filed of the rest of the molecule and it should be assumed for a moment that it could only move in the direction of the zigzag line connecting C and N atoms in the chain. The potential energy of the electron is then roughly constant along the chain. Since the electron is practically in the coulomb field of the nearest C and N atom only, while the field of more distant C and N is neutralized by other pi electrons. And, consequently, this electron can move almost freely along the zigzag line, but not beyond the ends of the chain except when the chain itself stretches. Thus, this electron is in the same condition as a free electron considered earlier in a one-dimensional box and the length L of the chain corresponds to the length of the box. It must be noted, however, that the component of the motion of the pi electron in the direction perpendicular to the zigzag line connecting C and N atoms in the chain has been neglected here (XIIb).

In the normal state of the molecule, the three electron pairs present in the resonating chain occupy the three lowest levels. The light absorption is caused by transition of an electron from the highest occupied molecular orbital (HOMO) with n = 3 to the lowest unoccupied molecular orbital (LUMO) with n = 4. Accordingly, the energy difference ΔE between these states is,

$$\Delta E = E_4 - E_3 = (4h)^2/8mL^2 - (3h)^2/8mL^2 = 7h^2/8mL^2 = 6.1\times10^{-12} \text{ ergs}$$

$$\text{And, } \lambda_{\mathbf{max}} = hc/\Delta E = (6.624\times10^{-27})(2.998\times10^{10})/6.1\times10^{-12}$$

$$= 3.3\times10^{-5} = 330\text{nm}$$

This value is in good agreement[144] with the experimental value of 313nm. As another case, let us discuss a specific dye, 1,1'- diethylcyanineiodide (cryptocyanine): figure XV. The cation can resonate between two limiting

structures, which really means that the wave function for the ion has equal contribution from both states. Thus, all the bonds along this chain can be considered as equivalent, with bond order of 1.5 similar to C-C bond in benzene. Each carbon atom in the chain and each nitrogen atom in the ends are here involved in bonding with three atoms by three localized bonds, so the called sigma-bonds. The extra valence electrons on the carbon atoms in the chain and the remaining three electrons on the two nitrogen atoms form a mobile cloud of pi electrons along the chain and extend above and below the plane of the chain. We then, assume that the potential energy is constant along the chain and that rises sharply to infinity at the ends; that is the pi electron system is replaceable by free electrons moving in a one dimensional box of length L, for example, if it is supposed that total number of pi electrons in this system be N, then as said before, for electron transition and consequent light absorption, the transition energy and the wavelength of maximum absorption can be arrived at as in equation E.2 and E.3 respectively. To reproduce the latter,

$$\lambda = 8mcL^2/h(N+1) \qquad \text{E.3}$$

The number of carbon atoms in polymethine chain, if supposed, are p, then N=p+3. Kuhn assumed that l was the length of the chain between nitrogen atoms plus one bond distance on each side; thus, L=(p+3) I where I is the bond length between atoms along the chain. Therefore,

$$\lambda = 8mcL^2(p+3)^2/h(p+4) \qquad \text{E.4}$$

Putting $I = 1.39\times10^{-8}$ cm (the bond length of benzene, a molecule with similar bonding) and converting from centimeters to nanometers ($1nm=10^{-9}m$), we find,

$$\lambda\,(\text{in nm}) = 63.7(p+3)^2/\,(p+4) \qquad \text{E.5}$$

If there are easily polarizable groups at the ends of the chain, such as benzene rings, the benzene, the potential energy of the pi electrons in the chain doesn't rise so sharply at the ends. In effect, this lengthens the path L, and we can write,

$$\lambda\,(\text{in nm}) = 63.7\,(p+3+\alpha)^2/(p+4) \qquad \text{E.6}$$

Where α should be constant for a series of the dyes of a given type. If such a series is studied experimentally, this empirical, α, may be adjusted to achieve the best fit the data; in any event, should lie between 0 and 1 [145].

In order to compare the result of this method with the more sophisticated Valence bond (VB) or the molecular (MO) calculations, let us use equation 5 which assumes that $\alpha=0$, to calculate the wave length of maximum absorption of cryptocyanine, in which p=9 and compare that value with those given by others in literature [146]

Free electron	= 707 nm
Bond orbital (case 1)	=3900 nm
Bond orbital (case 2)	=2900nm
Molecular orbital	=2700nm

It may be noted that only FEM predicts an absorption band in the visible region of the spectrum in agreement with the actual observation. Kuhn has applied this method to the determination of the wavelength of maximum absorption of a number of cyanine dyes with varying values of α, whose classical structures are depicted in figure XVI. Both structures are equivalent. The potential energy of the well of the model is not, however, constant due to the presence of two nitrogen atoms. The number of atoms in the conjugated chain is 2a+9 and since the potential energy barrier extends beyond the terminal nuclei by about one bond length, the number of pi electrons N is 2a+10, each carbon atom contributes one electron and two terminal atoms together contribute three electrons. Since the C-C bond distance is known, the total length, L, of the well can be calculated. The individual bond distance is taken as 1.39×10^{-8} cm, i.e. the C-C bond distance in the benzene molecule. Table 2 summarizes the calculated values of λ_{max} which are in good agreement with the experimental values by Brooker[147] over the range where a, the number of vinyl groups, increases from zero to three.

TABLE 2

POSITIONS OF ABSORPTION BANDS IN THE SPECTRA OF CYANINE DYES

A	a	λ_{max} (calc.)[148] nm	λ_{max} (observed)[147] nm
	0	579	590
	1	706	710
	2	834	820
	3	959	930

The agreement is good considering that the terminal benzene rings are not included in the calculations. By using linear compound similar to cyanine dyes in structure but not containing benzene ring, i.e. those of the general structure,

$(CH_3)_2\ N^+ = CH\text{-}(CH = CH)_a - N(CH_3)_2$

Where the value of a is 1, 2, or 3, Simpon[149] has found excellent agreement between observed and the calculated values of $\lambda_{max.}$ The total number of pi electrons is (2a + 4) including again a contribution of three electrons from the nitrogen atoms. With a reasonable estimate of the length of the potential well, values of λ_{max} shown in table 3 were obtained.

<u>Table 3</u>

a	Calculated λ_{max} nm	Observed λ_{max} nm
1	309	309
2	409	409
3	509	511

A symmetrical cyanine dye with m conjugated double bonds in the resonating chain connecting the two nitrogen atoms. The number of pi electrons in the chain amounts to 2m+2, and the absorption band corresponds to a jump of electron from the HUMO level m+1 to the LUMO level m+2. as before the energy for this transition:

$$\Delta E = h^2(m+2)^2/8m_eL^2 - h^2(m+1)^2/8m_eL^2 = h^2(2m+3)8m_e L^2 \quad \text{and}$$
$$\lambda_{max} = hc/\Delta E = m_ec/hL^2/(2m+3) \qquad \text{equation...7}$$

This remarkable result in this approximation indicates that the position of the absorption band is determined by the chain length and by the number of pi electrons 2m+2, since m_e, the mass, h, the Planck's constants and c, the velocity of light are universal constants. Further λ_{max} does not depend upon any specific property of the atoms along the chain. The length L, may be taken as equal to $2m \times I$ where I is bond length of the chain elements; the average bond length, I, has taken as 1.3 angstrom on the basis of approximations considered by Kuhn[150-151]. The electron gas stretches by length, αL, on both sides of the each terminal nitrogen atom. Thus, a more satisfactory value of L is given by

The agreement is good considering that the terminal benzene rings are not included in the calculations. By using linear compound similar to cyanine dyes in structure but not containing benzene ring, i.e. those of the general structure,

$(CH_3)_2\,N^+ = CH\text{-}(CH = CH)_a - N(CH_3)_2$

Where the value of a is 1, 2, or 3, Simpon[149] has found excellent agreement between observed and the calculated values of $\lambda_{max.}$ The total number of pi electrons is (2a + 4) including again a contribution of three electrons from the nitrogen atoms. With a reasonable estimate of the length of the potential well, values of λ_{max} shown in table 3 were obtained.

Table 3

a	Calculated λ_{max} nm	Observed λ_{max} nm
1	309	309
2	409	409
3	509	511

A symmetrical cyanine dye with m conjugated double bonds in the resonating chain connecting the two nitrogen atoms. The number of pi electrons in the chain amounts to 2m+2, and the absorption band corresponds to a jump of electron from the HUMO level m+1 to the LUMO level m+2. as before the energy for this transition:

$$\Delta E = h^2(m+2)^2/8m_eL^2 - h^2(m+1)^2/8m_eL^2 = h^2(2m+3)8m_e L^2 \quad \text{and}$$
$$\lambda_{max} = hc/\Delta E = m_ec/hL^2/(2m+3) \qquad \text{equation...7}$$

This remarkable result in this approximation indicates that the position of the absorption band is determined by the chain length and by the number of pi electrons 2m+2, since m_e, the mass, h, the Planck's constants and c, the velocity of light are universal constants. Further λ_{max} does not depend upon any specific property of the atoms along the chain. The length L, may be taken as equal to $2m \times I$ where I is bond length of the chain elements; the average bond length, I , has taken as 1.3 angstrom on the basis of approximations considered by Kuhn[150-151]. The electron gas stretches by length, αL, on both sides of the each terminal nitrogen atom. Thus, a more satisfactory value of L is given by

$$L = 2m \times l + 2\alpha \times l = 2l \times (m+\alpha)$$

Now according to eqn. 7

$$\lambda_{max} = 8m_e c/h \times 4l^2(m+\alpha)^2/(2m+3)$$
$$= 127(m+\alpha/2)^2/(m+3/2) \text{ nm} \qquad \text{Equation ......8}$$

In the conjugation polyenes, symmetrical cyanines and their analogues. Kuhn[152] has calculated the stretching of the electron gas to both sides of each terminal atom, as 1.5 angstrom, on the basis of vibration treatment. As the length αL on both the ends is approximately 1.5A. This may be considered that α=1. the value α=1 has already been used of α is the treatment of the dye molecule, F.XVII. It has been found that the value of α is dependent on the end groups, and thus in a homologous series of dyes α is constant for all the members of the series. If strongly polarizable groups in increasing orders are introduced in the terminal atoms, the value of α also increases. On the basis of above considerations the calculated value λ_{max} of the said dye with m=2,3,4,5,6 and 7 are in excellent agreement with experimental data[153] of these carbocyanines.

The free electron method has also been used[154] to determine longest wavelength of absorption of a number of basic dyes and to compare the influence of a central nitrogen a tom in a conjugated system. In the simplest case the linear compound A is compared with the aza derivative B in which the central carbon atom has been replaced by nitrogen. This atom contributes one electron to the total pi system and since it is more electronegative than carbon atom that it replaces, there will be decrease in the HOMO energy level in the ground state.

$(CH_3)_2\overset{(+)}{N}=CH-CH=CH-N(CH_3)_2$, $(H_3C)_2\overset{(+)}{N}=CH-N=CH-$
$-N(CH_3)_2$

A B

In the first excited state of both A and B, there is vibration node at the central atom and the energy level in both the cases is equivalent. Consequently the excitation energy ΔE involved in the transition will be greater for azo derivative, which therefore possesses a λ_{max} at a shorter wavelength. In general, when centrally situated –CH= group is replaced by –N= in a resonating system between terminal nitrogen atoms, a hypsochromic shift is observed if there is an even number of double bonds

and a bethchromic shift is seen when the number of double bonds is odd. This is because the value of the energy levels in the excited state depends on presence of a node or an anti node at the central atom.

The displacement of a given energy level caused by the nitrogen substitution may be quantitatively assessed by a perturbation treatment and is given by the equation.

$\Sigma = \mathbf{A}\Psi^2$ Equation ...9

Where A is an electronegativity constant, characteristic of the heteroatom and is equal to 3.9×10^{-20} erg cm for the – N = atom, Ψ is the normalized wave function at the heteratom. It can be shown that 2/L give the square of the normalized wave function, where L is again the length of the potential well. It follows that for a state with an anti node at the central atom.

$\Sigma = - Ax^2/ L = -2A/2(M + \alpha)l$ Equation 10

Where M is the number of double bonds and is the mean carbon – carbon bond distance. The factor α is introduced, as said before, to account for the extension of constant well potential beyond the terminal atoms of the conjugated system.

The potential well diagram of the simplified free electron model is modified by the presence of electronegative atom to that shown in figure XVIII.

The nitrogen atom is situated at the center of the well and where b, the mean C—N distance, is small compared to the total well length, the probability of finding electron in the trough is Ψ^2b. The reduction, ε, in the total energy of the state n is, therefore, $-V\Psi^2$b where V is the negative potential due to the nitrogen atom. It follows from equation 9 that A = Vb or in other words the electronegative constant is the product of the potential energy drop and the bond distance between the hetero atom and its neighbor.

A comparison of the spectra of Michler's Hydrol Blue and Bindschedler's Green, the structures of which are shown in figure XIX, shows that the observed value of $\lambda_{\mathbf{max}}$ are 603 and 725 nm respectively. If the Δ**E'** is the excitation energy of the aza dye, then,

$\Delta\mathbf{E'} = \Delta\mathbf{E} + \Sigma$ equation ...11

for the excited state possessing a central antinode the $\Delta E'$ is the excitation energy of the parent unsubstituted molecule (a) in the said figure and

$$E = hc/\lambda_{max} = 6.62x10^{-27} \text{ x } 3.00 \text{ x } 10^{10}/6.03 \text{ x } 10^{-5}$$
$$= 3.30 \text{ x } 10^{-12} \text{ erg}$$

in equation 11 can be calculated from equation 10 since the values of all the constants, with the exception of α are known. This factor α may be determined by calculating the value of L when observed value λ_{max} for the parent molecule is substituted in equation 3. Comparison of this value of L with the value calculated from the number of double bond and the mean bond length, as shown by Kuhn[154], gives $\alpha = 0.55$. The number of double bonds is five from equation 10,

$$\varepsilon = -(3{,}9 \text{ x } 10^{-20}/(5+0.55)(1.39X10^{-8})$$
$$= -0.5x\ 10^{-12} \text{ erg}$$

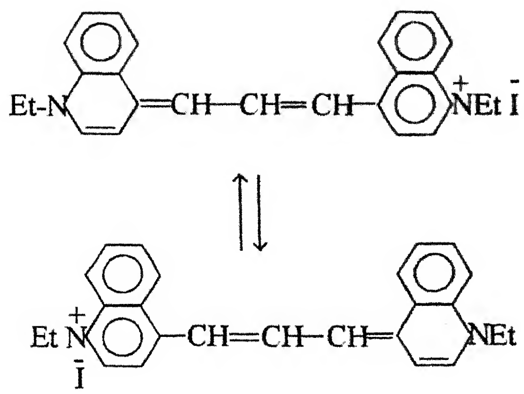
The values of $\Delta E'$ is the sum of these energy terms.

$$\Delta E' = 3.30x10^{-12} - 0.5x10^{-12}$$
$$= 2.80x10^{-12} \text{ erg}$$

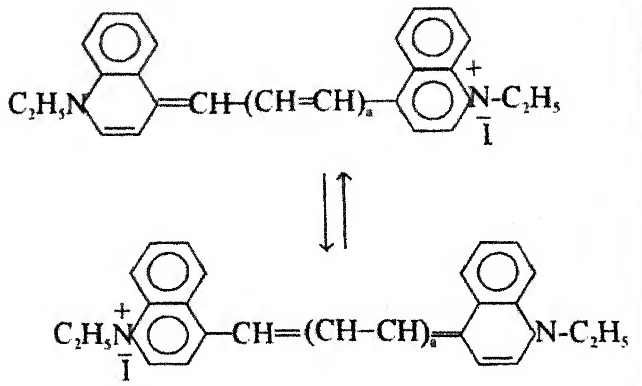
Expressing this energy in wave length terms give a wave length of maximum absorption for Bindschedler's Green (figure XIXb) at 709 nm, a calculated shift of 106 nm, in reasonable agreement with the observed shift of 122 nm on replacing the central –CH = group. Similarly, Michler's Hydrol Blue may be compared with Acridine Orange, figure XX.

The electronegativity constant for A for $N - CH_3$ at the position 12 in this compound is $6.0x10^{-20}$ erg cm. In the normal state of the molecule the seven pairs of pi electrons, contributed from the five double bonds and uncharged nitrogen atoms, fill the seven highest occupied energy levels. A free electron model treatment as above gives a calculated value λ_{max} for acridine orange of 471 nm compared with an observed value of 491 nm. The absorption spectra of acridine, oxazine, thiazine, azine and xanthene dyes have all been compared by this method[154] with some degree of success.

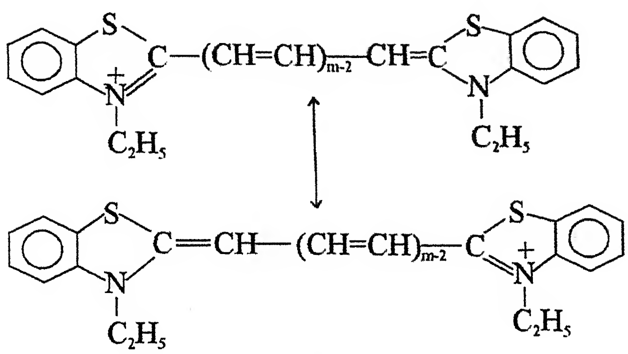
Equation 3 predicts that the absorption band with the lowest energy should be displaced to longer wavelength when an increasing number of ethylenic linkages is introduced into the molecule since L^2 is proportional to the wave length. However, with linear polymers, the wavelength of



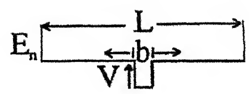
XV



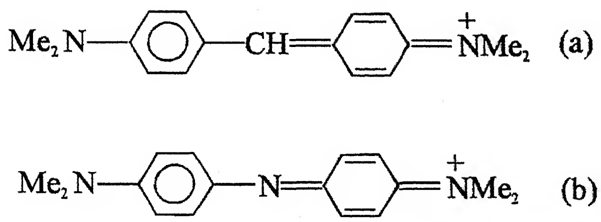
XVI



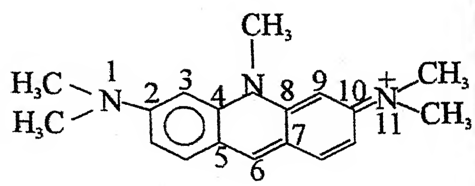
XVII



XVIII

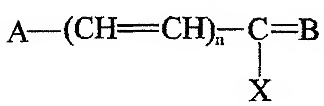


XIX

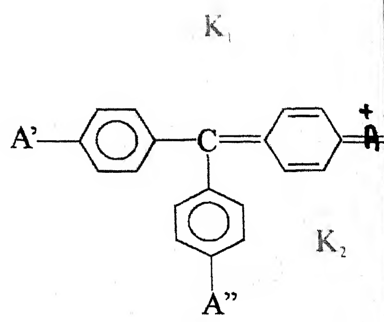


Acridine Orange

XX



XXI (a)



XXI (b)

absorption tends to a maximum as the number of double bonds is increased. The assumption of a constant pi electron potential in the simple free electron model has been shown[155] to be incorrect and a regular variation in bond length occurs along the chain if it is sufficiently long. Such a varying energy along the box increase the gap between the occupied and the unoccupied orbital so that λ_{max} tends to limit the chain length increases. In terms of resonance theory explanation is that in long chains of this type, the number of idealized structures contributing to the stability of the excited state increases to a greater extent than the contribution each makes to the stability of the ground state. Consequently, the energy difference increase with the increasing chain length.

The FEMO theory has certain feature in common with the qualitative interpretation of the special shifts associated with Burawoy's K-band theory[156] in triarylmethane dyes and thiobenzenophenone derivatives[157], particularly in its application to the basic dyes, where the electronegative atom situated in a conjugated system can act as an electron sink. The intense K-bands (Burawoy's nomenclature – K-konjugierte) are attributed to $\pi \rightarrow \pi^*$ excitation when a conjugated molecule contains both an electron donating and electron withdrawing group, a shift of the K-band to a longer wave length occurs which is greater than the additive effect of both group when acting separately. Changes in the nature of the terminal groups in such systems which cause an increase in polarity or polarizability, or the dissolution of the compound in more polar solvents, cause further shift of the K-bands to the longer wavelengths. The presence of the side chain groups also effects the position of the K-band, opposing the electron migration from terminal groups, e.g. from A to B in figure XXIa, where A and B may be $N(CH_3)_2$ and $= N^+(CH_3)_2$ respectively and assisting it in the new system of groups X (which may be e.g. OH or $-NH_2$) and group B. This replacement of K-band is therefore to shorter wavelength with thiobenzene and triarylmethane cations which are symmetrically substituted, the side chain is also conjugated. The absorption spectra show only one band but should in fact consist of two superimposed bands, i.e. originating from K_1 and K_2 in figure XXIb.

These bands become apparent when the absorption spectra of non-symmetrically triarymethane chromophores are examined. When A, A' and A'' are identical and are either $-OCH_3$, $-SCH_3$ or $-NCH_3$, (Crystal Violet) then only one band is observed at 480, 577 and 587 nm respectively. Replacement of one subtituents in each of these compounds by hydrogen, (e.g. changing crystal violet to malachite green) cause the emergence of a second band K_2 at shorter wavelengths. Simultaneously,

the K_1- band undergoes a bathchromic shift of between 20 and 40 nm. Lewis and Bigeleisen[158] have also made similar observations for crystal violet and the sodium salts of Rhodamine B and Fluorescein.

Kuhn has used the branched pi electron gas model to treat other dyes in a similar manner and the concept of branching leads to a simple explanation of even such characteristic compounds as deep colour of the low molecular weight Wurster's Blue and azulene[159].

It is of interest to consider the application of the free electron theory to closed ring systems having conjugation similar to that occurring in porphyrins, azaporphines and phthalocyanines. The free electron theory has been applied to the metal free porphins[160], cyclic polyenes[161] and phthalocyanines[162-163], using a circular box model, and by taking into account the perturbation factor calculated from atomic shielding constants[164], better agreement[165] has been found with the experimental data[166].

Labhart[167] further refined free electron theory by taking into account the interaction between the pi electrons and the elastic sigma skeleton. He showed that even for very long polyenes a difference in single and double bond length was of the same order of magnitude as in shorter polyenes was to be expected. Olszewaki[168] used a linear free electron model with electron-electron and electron-core interaction for the calculation of lowest excited singlet-triplet separation in polyenes, twisting frequency of ethylenes and location of absorption maxima in cumulenes. He also calculated the absorption maxima in the spectra symmetrical cyanine dyes and polyenes by ASFEMO-Anti-Symmetrical Free Electron Molecular Orbital method. An improvement of the theoretical λ_{max} values for cyanines was obtained by introducing resonance barrier[169] in the free electron model. Spectra of cyanine dyes and cata-condensed hydrocarbons were analyzed by Araki and Huzinaga[170-171], Basu[172], Dey[173] and by Rout et al[174]. who applied suitably modified FEMO method. A part from spectral analysis, the refined FEMO has also been used for the calculation of optical rotatory power[175] of the organic molecule. The model gave a method for rapid evaluation of electric and magnetic transition moments and was further used for a better understanding of the skew conformation of butadiene. Shuler[176] used the free electron model for calculating the stability constants and absorption spectra of pi molecular complexes. Mueller[177] examined theoretically the bimolecular exchange reaction.

$H_2 + H_2 \rightarrow \quad H_2 +$ and $H + H_2 \quad \rightarrow \; H_2 + H$

Via activated complex by free electron model. Bonham et al[178]. and Basu[179] treated the electrophilic substitution in molecules by the FEMO method. The treatment is based on the fact that any aromatic substitution reaction proceeds through the formation of the activated complex. Nathan[180] successfully employed the FEMO method for the theoretical investigation of diamagnetism of aromatic hydrocarbons.

B.8 TWO DIMENSIONAL FREE ELECTRON GAS MODEL :

The two-dimensional free electron gas model[183] is closely related to the branched electron model described earlier in this chapter. Each state of interest in the two dimensional model corresponds to a state in the one-dimensional model. In the two dimensional model for a system with resonating structure, the plane of the center of the atoms is chosen as the xy-plane of the xyz-coordinate system. It is assumed that the pi electrons are in potential field V(z) + V(xy), where V(z) is a certain function of z. V(xy) is the potential of the pi electron averaged over z and is the sum of the contributions of the carbon atoms. The contribution of the carbon atom can be obtained by nuclear charge and shielding considerations. The z part of the wave function of an electron in the potential V(z) + V(xy) can be separated from the xy part, and the problem of finding eigen functions ϕ_n (x,y) and eigen values E_n of the Schrodinger wave equation.

$$\delta^2\psi_n/\delta x^2 + \delta^2\psi_n/\delta y^2 + 8\pi^2 m\,[E_n - V(x,y)]\,/h^2 = 0$$

can be solved by using an analog computer. The two dimensional method can be applied to polyenes and polyacetylenes. Using the observed values of bond distances, the position of the strong absorption bands was calculated and the results were found to be in good agreement with those of one-dimensional treatment and with the observed data[184]. Two dimensional models may also be applied to dye molecules of any complicated shape.

C.PHTHALEINS: THEIR COLOUR AND CONSTITUTION:

An entirely different series of dyes, the phthalein dyes, figure XXIII, XXIV and XXVI may be obtained by simply replacing $N-CH_3$ by more electronegative oxygen atom at the position 12 H at position 6 by $-C_6H_5COO^-$ in acridine orange figure, XX. Derivative of pyronines, these phthaleins may be considered to be intermediates between fuschone Figure XXII and benzaurine figure XXV.

Colour responsibility of these acid dyes, the phthaleins, is attributed to the anionic portion, which thus becomes more important part of the dye molecule. It has been established for a well studied representative of the phthalein, that in the neutral medium it bears a lactone structure and thus is then colourless, figure XXVI, while in alkaline solution (pH 8.4) it undergoes ring opening producing intense red divalent anion, figure XXVII, having longest wave length band of λ_{max} at 532 nm with an extinction coefficient of 31,000. further, the well known property of phenolphthalein as an indicator is λ_{max} actually attributed to this very intense red divalent anionic form which actually is a hybrid of figure XXVIII and a number of its possible intermediate resonating structures. The divalent anion transforms to carbinol, figure XXX, a trivalent anion, when excess alkali is added, and thus loses the colour.

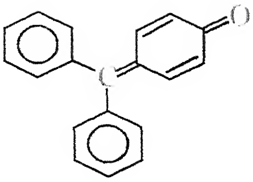
An analogue of phthalein is fluorescein, figure XXIII that differs only in the presence of an oxygen bridge. Both phenolphthalein and fluorescein in alkaline medium exhibit bathchromic shift. In each case, alkali produces an ion that can be represented by two equivalent resonating structures. Thus the alkali produces ions that are stabilized by resonance and this leads to absorption at longer wavelengths. Fluorescein has two equivalent resonating structures shown in XXXIa and XXXIb in the alkali medium.

Fluorescein, as expected, absorbs at shorter wavelengths than phenolphthalein. The flurorescein anion is red (λ_{max} in water 500nm) where as phenolphthalein anion is magenta (λ_{max} in water 552nm). Fluorscein absorbs at shorter wave length because in it, charge distribution between two oxygen atoms is decreased due to the oxygen bridge of the pyrone ring, which is capable of forming a double bond with the ring acquiring some of the available charge. Fluorescein is characterized by a strong green fluorescence and many of its derivatives are also fluorescent.

Eosin, figure XXXII, having bromine atoms at ortho positions to pyrone oxygen, electron density of carbon atoms of pyrone is increased and consequently it hinders oxygen to take up part of the oscillating charge. It is evident from the structure of phthalein, figure XXVII and XXIX and also from the above considerations that only part of the molecule which is shown above the dotted line plays important part in the light absorption as regards the main absorption band of the molecule. The removal of the carboxyl group in the compounds, figure XXXIII to XXXVI doesn't affect the position of the absorption maxima in compounds, figure XXXVII to XL. A number of workers[185-205] have studied the effect on light absorption by making changes in lower part

(below the dotted line) of the molecule figure XXIII and XXVI, and could find so significant changes in λ_{max} thus confirming the previous observations. Ghatak and dutt[206] have prepared phthaleins of the type XLI in which two hydroxyl molecules are dissimilar. They also prepared asymmetric fluoresceins where the substituents in the two sides of the fluoron nucleus are not identical, figure XLII and XLIII.

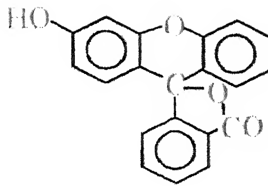
Recently, Gupta, Beg, Ali et al. have prepared and studied the chemistry of some novel analogues of phthalein and succinein dyes; specially their synthesis and colour. The present investigations are in continuation of the work that has already been done by Beg et al.



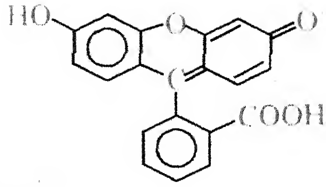
Fuschone

λ_{Max} 309 nm

XXII



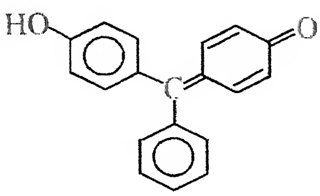
XXIII



Flureoscein

λ_{Max} 495 nm

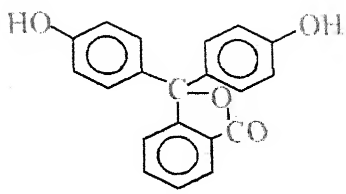
XXIV



Benzaurin

λ_{Max} 530 nm

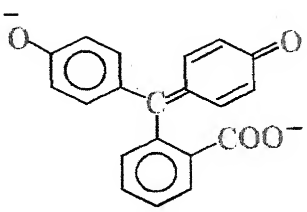
XXV



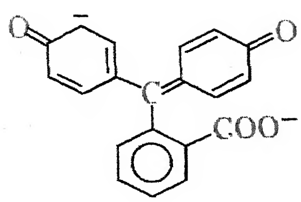
Phenolphthalein

λ_{Max} 532 nm

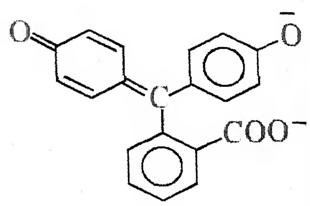
XXVI



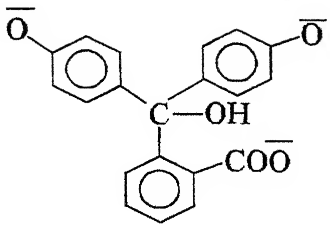
XXVII



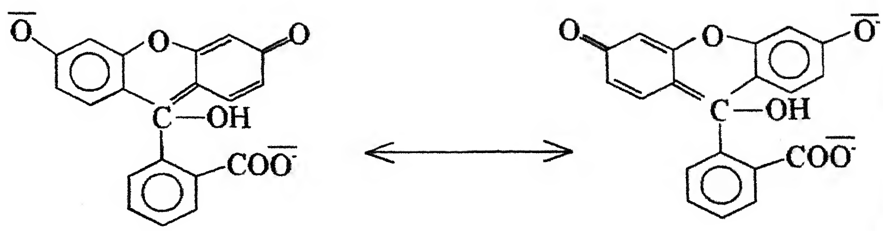
XXVIII



XXIX

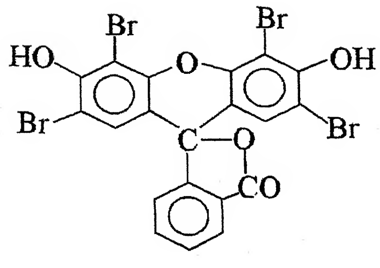


Trivalent *anion*
(A carbinol derivative)
XXX

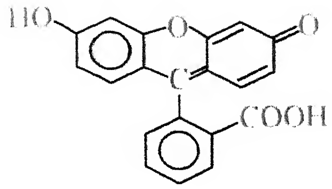


Fluorescein

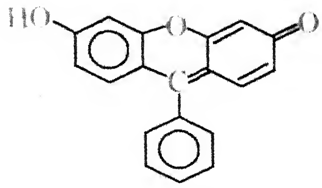
XXXIa XXXIb



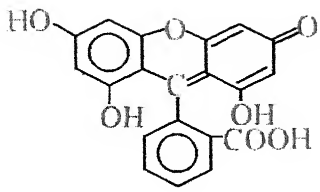
XXXII Eosin



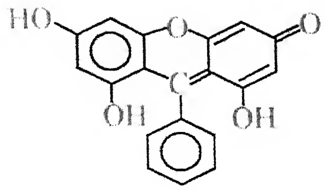
XXXIII 500 nm



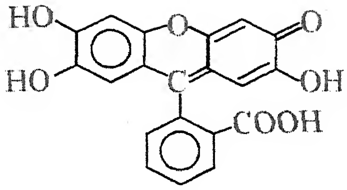
XXXVII 500 nm



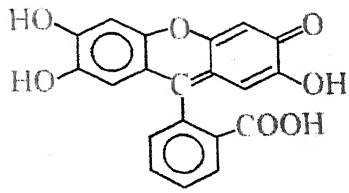
XXXIV 498 nm



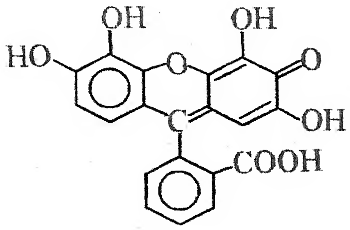
XXXVIII 498 nm



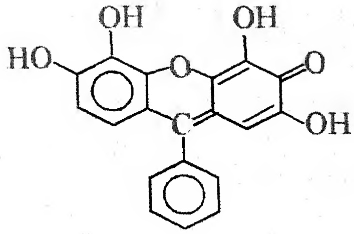
XXXV 554 nm



XXXIX 554 nm



XXXVI 598 nm



XL 598 nm

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CHAPTER

TWO

RESULTS & DISCUSSION

CHAPTER II

RESULTS AND DISCUSSION

From the foregoing discussion contained in the first introductory chapter, it is obvious that if a change is to be made in the frequency of the first absorption band, it is futile to tackle the acid part in the resonance of the molecule, but at the same time it has been observed that alteration in the number of auxochromes, their position and nature in resonating part produces a marked effect on $\lambda_{max.}$ It has already been described that two quinonoid forms XXVII and XXIX in the alkaline medium can represent the lactone form of phenolphthalein. Thus, if a condition could be created to accomplish radical alteration in molecule by replacing one of the hydroxyl aromatic nuclei by an alkyl or an aryl group or by a heterocyclic ring, the resonance in the phenolphthalein nucleus is rendered possible in one of the two quinonoid form mentioned above and the colour development of the substance will be expected to be much less intense than in the case of phenolphthalein. To study this effect of the above planned alterations in the upper part (non acid) of the phthalein molecule, twelve γ-keto acids (series A,B,C) were prepared and condensed with various aromatic hydroxyl compounds to get novel analogues of the phthaleins.

To see the effect of the lower acid part in the colour of the dye, four β-aroyl propionic acids (series D) were also prepared and condensed with various phenolic compound to get novel analogues of succcineins i.e. succin-as-eins. General structure of phthal-as-eins and succin-as-eins prepared are given by XLV A and B respectively.

ACIDS OF SERIES A

1. 2-(2' 4' dimethyl benzoyl) benzoic acid
2. 2-(3' carbmethoxy 4' hydroxy benzoyl) benzoic acid
3. 2-(5' chloro 2' chloromethyl benzoyl) benzoic acid.
4. 2-(3' acenaphthoyl) benzoic acid

ACIDS OF SERIES B

1. 2-(2' 4' dimethyl benzoyl) tetrachlorobenzoic acid

2. 2-(3' carbmethoxy 4' hydroxy benzoyl) tetrachlorobenzoic acid

3. 2-(5' chloro 2' chloromethyl benzoyl) tetrachlorobenzoic acid.

4. 2-(3' acenaphthoyl) tetrachlorobenzoic acid

ACIDS OF SERIES C

1. 2-(2' 4' dimethyl benzoyl)-3- nitrobenzoic acid

2. 2-(3' carbmethoxy 4' hydroxy benzoyl)- 3- nitrobenzoic acid

3. 2-(5' chloro 2' chloromethyl benzoyl)- 3- nitrobenzoic acid.

4. 2-(3' acenaphthoyl)- 3- nitrobenzoic acid

ACIDS OF SERIES D

1. β -(2, 4 dimethyl benzoyl) propionic acid

2. β -(3 carbmethoxy 4 hydroxy benzoyl) propionic acid

3. β -(5 chloro 2 chloromethyl benzoyl) propionic acid.

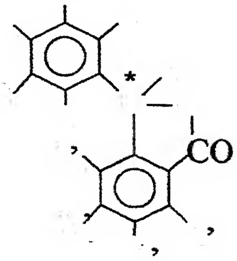
4. β -(3 acenaphthoyl) propionic acid

The nomenclature of these dyes has been arrived at by considering the asymmetry in the structure of the molecule. These may be regarded as mixed or unsymmetrical phthaleins XLV-A as derivatives of phthalide, and unsymmetrical succineins XLV-B. For convenience and uniformity, and owing to the asymmetric carbon (C) present in all, the more satisfactory nomenclature for XLV-A and XLV-B is adopted, and the compounds are named as follows:

Phthal-as-eins, Succin-as-eins, as representing asymmetry, ein representing the class of dyes (Phthalein or succinein).

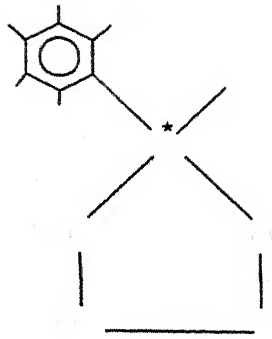
STRUCTURE OF PHTHAL-AS-EINS:

On the basis of study of the chemical constitution of these XLV-A dyes



Phthal-as-ein

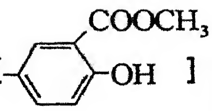
XLV A

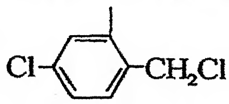
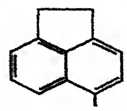


Succin-as-ein

XLV B

For dyes derived from series A, B, C and D :

R = 2, 4 dimethyl phenyl ($-C_6H_3(CH_3)_2$) ; 3 Carbmethoxy 4 - Hydroxy phenyl []

2 Chloromethyl, 5 Chlorophenyl [] ; 3 - acenaphthyl []

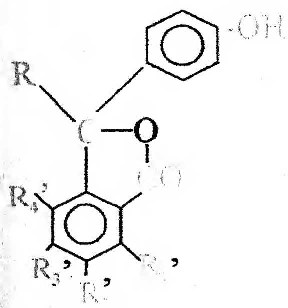
$R_1, R_2, R_3, R_4, R_5,$ = H or OH; $R_2 = R_4$ = H or Br

$R_1 = R_3 = O.OC\text{-}CH_3$

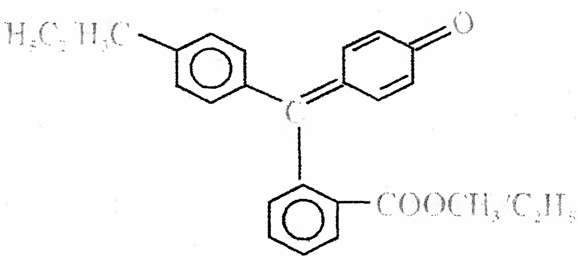
$R_1' = R_2' = R_3' = R_4'$ = H (for dyes derived from series A)

$R_1' = R_2' = R_3' = R_4'$ = Cl (for dyes derived from series B)

$R_1' = R_2' = R_3'$ = H; $R_4' = NO_2$ (for dyes derived from series C)



XLVI



XLVII

$R_1' = R_2' = R_3' = R_4'$ = H OR Cl

$R_1' = R_2' = R_3'$ = H; $R_4' = NO_2$

(discussed in the preceding section) structure XLVI has been assigned to phenol-phthal-as-eins.

It may be noticed that the assigned structure of phenol-phthal-as-ein XLVI is similar to dimethy[11] and diethy[12] XLVII derivative of phenolphthalein. In these derivatives, there seems the possibility of the same type of resonance to occur as exhibited by phenolphthalein itself. In the same way the resonance of phenolphthalein type will be altogether absent in XLVI.

The anologue of dimethyl derivative is orange red and the corresponding diethyl derivative is yellow even in the solid state.

SERIES A:

The representative dyes of this series are the following:

1. 2, 4 dimethyl phenyl phenol phthal-as-ein.

2. 3 carbmethoxy 4 hydroxy phenyl phenol phthal-as-ein.

3. 5 chloro 2 chloromethyl phenyl phenol phthal-as-ein.

4 3 acenaphthyl phenol phthal-as-ein.

The above four dyes are brown, dark brown, brown and reddish brown respectively.

SERIES B:

The representative dyes of this series are the following:

1. 2, 4 dimethyl phenyl, phenol tetra chloro phthal-as-ein.

2. 3 carbmethoxy 4 hydroxyl phenyl phenol tetra chloro phthal-as-ein

3. 5-chloro 2 chloromethyl ~~5-chloro~~phenyl phenol tetra chloro phthal-as-ein.

4. 3- acenaphthyl phenol tetra chloro phthal-as-ein

The above four dyes are pale rosy ,pinkish white, light red and rosy respectively.

SERIES C:

The representative dyes of this series are the following.

1. 2, 4 dimehtyl phenyl phenol nitro phthal-as-ein.

2. 3 carbmethoxy 4 hydroxyl phenyl phenol nitro phthal-as-ein.

3. 5 chloro 2 chloromethyl phenyl phenol nitro phthal-as-ein.

4. 3 acenaphthyl phenol nitro phthal-as-ein.

The above four dyes are pinkish red, light pink, pinkish white and light pink respectively.

SERIES D:

The representative dyes of this series taken are as follows:

1. 2, 4 dimethyl phenyl phenol succin-as-ein.

2. 3 carbmethoxy 4- hydroxyl phenyl phenol succin-as-ein.

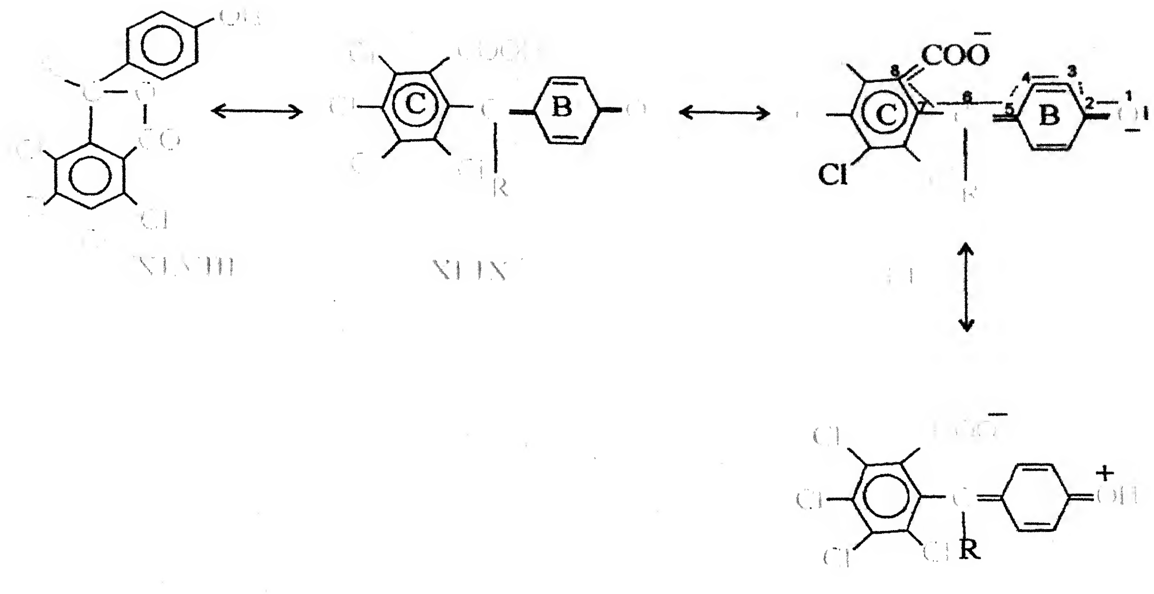
3. 5 chloro 2 chloromethyl phenyl pbenol succin-as-ein.

4. 3 acenaphthyl phenol succin-as-ein.

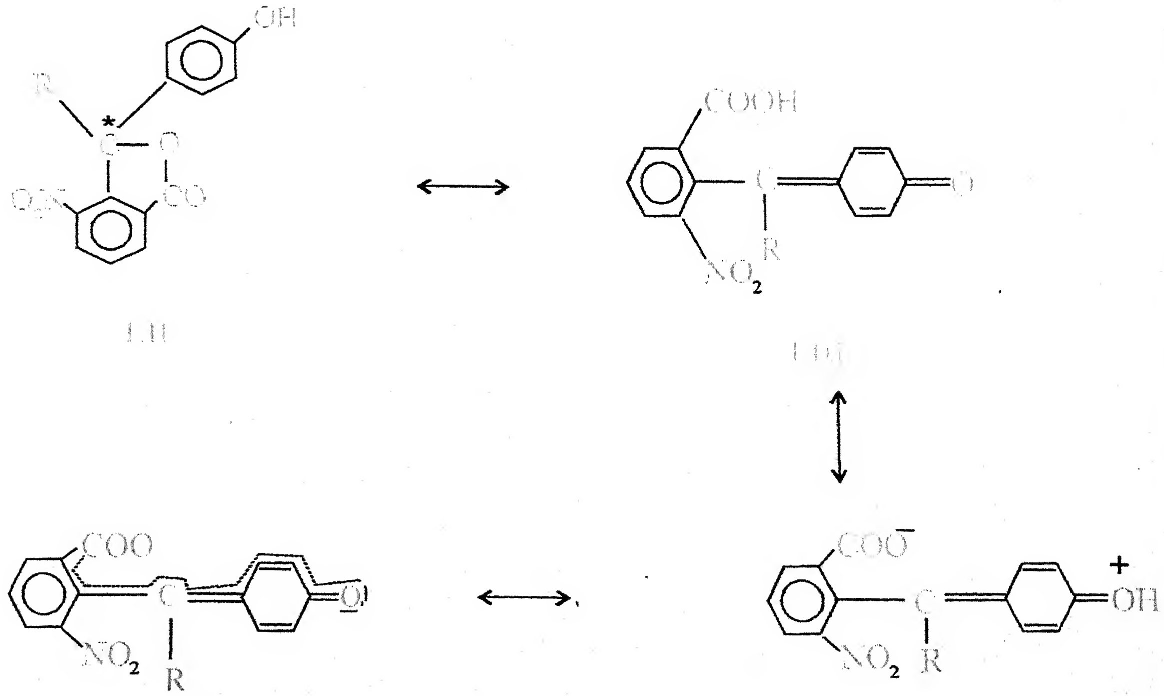
The above four dyes are leaf-brown, brown, gulf-red and leaf green respectively. The colour of these phenol phthal-as-ein dyes in neutral as well as alkaline medium and their $\lambda_{max.}$ values, are given in tabular form at the end of this thesis.

The colour of phenol phthal-as-eins may be explained, as already discussed, and interpreted in chapter I.

The colour of phenol tetra chloro phthal-as-eins may be explained on the basis of resonance occurring among various neutral (XLVIII and XLIX) and polar (L and LI) structures of the molecules. Due to occurrence of resonance in the molecule, the presence of qunonoidal conjugation becomes possible in different participating structures and at he same time the formal charge is created in the polar resonating states in the basic medium. A symmetry of



XLVIII XLIX LI L

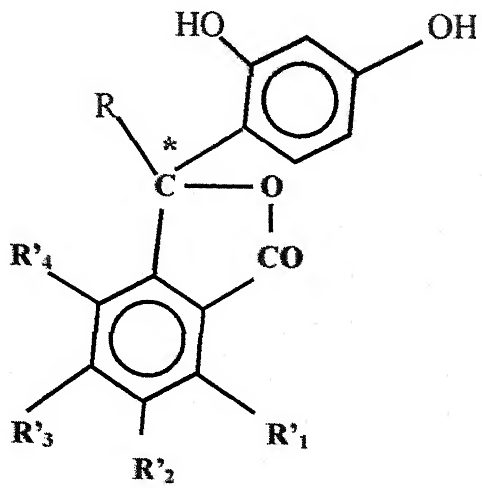


LII LIII LV LIV

phenolphthalein is altogether absent here but possibly the charge travels through the dotted lines (LI) and the absorption maxima is nearly the same as that of phenolphthalein (XXVII-XXIX) in moderate basic medium. The phenol tetra chloro phthal-as-eins studied here exhibit similar behaviour in basic medium as phenolphthalein The monovalent anion of phenolphthalein is colourless derivative, while the divalent anion (XXVII and XXIX) gives pink colour but the trivalent anion (XXX) is again colourless. In the same way the present phenol tetra chloro phthal-as-eins described in the thesis give pink colour in moderate basic medium and the disodium salts become almost colourless anions with strong acids show again the enhancement of colour (L).

Similarly, the colour of phenol nitro phthal-as-eins incorporated in the thesis may also be explained by considering the neutral (LII) and (LIII) and the polar (LIV) and (LV) resonating structures for the molecule.

The colour of the resorcinol phthal-as-eins (LVI) may be explained in relation to their chemical structures discussed in the preceding section on the basis of description in the case of phenol phthal-as-eins.



Resorcinol Phthal-as-in

LVI

In resorcinol phthal-as-eins, there are two hydroxyl groups (2:4 position) instead of one hydroxy group (4 position) in the hydroxyl aromatic part of the molecule (LVI). Out of the two hydroxyl groups, one acts as a chromophore to produce conjugation, while the other hydroxyl group acts as an auxochrome. Hence, even the neutral molecule can possible exist as a resonance hybrid of the LVI to LVIII structures. Thus, the colour of the resorcinol phthal-as-eins is well

accounted for either in solid state (yellow, yellowish orange, yellowish brown) as well as in neutral medium (λ_{max} 460-485 nm). However, by the addition of the alkali, the polar forms (LVIIa, LVIIIa, LVIIb and LVIIIb) of the molecule are produced resulting in increase in the number of resonating structures of the molecules. This increase is responsible for producing more crowded and depressed energy levels; consequently a bathochromic shift in λ_{max} takes place. Actually all these dyes have absorption bands at 460-485 nm in neutral medium while in slightly alkaline λ_{max} at 490-520 nm have been observed.

In most of the poly hydroxy phenol phthal-as-eins, one hydroxyl group takes part as the chromophore and rest of the hydroxyl groups present, may act as auxochromes causing a respective deepening of the colour of these dyes (appearance varies from yellow to dark brown). In some cases these dyes e.g. Hydroquinone, Catechol, Phloroglucinol and Pyrogallol phthal-as-eins have been found to decompose in alkaline medium. Due to this decomposition of dyes, reliable absorption maxima can not be determined. Hence, it is difficult to put forward a satisfactory explanation for their colour.

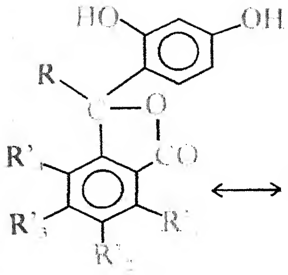
COLOUR OF SUCCIN-AS-EINS AND λ_{max} CALCULATIONS:

The λ_{max} value for various forms of succi-as-eins have been observed by some workers and it falls between 390-430 nm. In the present investigation, the succi-as-eins were prepared from four β-aroyl propionic acids. The various aryl phenol succi-as-eins are represented by the resonating structures LIX, LX and LXI which also explain their colour and λ_{max} (425-440 nm) here R = substituted phenyl and structure LXI makes a real contribution in alkaline medium. The dotted line indicates the possible path of travel of the electron along the conjugated chain. In this case it is not possible for conjugation to extend beyond the chiral carbon atom present at position 6 and the pi – electron gas consist of 8 electrons for four pi bonds (i.e. m = 4), out of which six electrons are contributed by three double bonds and two electrons by the charge free oxygen atom O1 (i.e. four pi bonds are contributed in the coulombic field). Stretching of electron gas is not at both ends, but only in one end i.e. $\alpha = \alpha/2$, hence from equation 8 of the first chapter.

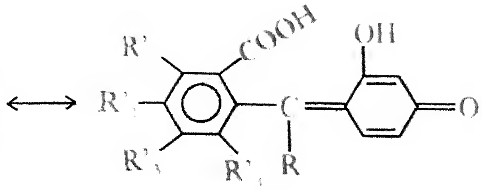
$$\lambda_{max} = 127(m + \alpha/2)^2/(m + 3/2)\ \text{nm}$$

$$= 127\ (4 + 0.33/2)^2 / (4 + 3/2) = 400\ \text{nm}$$

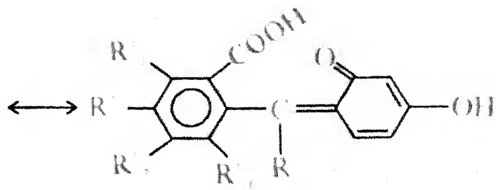
The λ_{max} observed is in the range of 425-440 nm. It may be noticed that



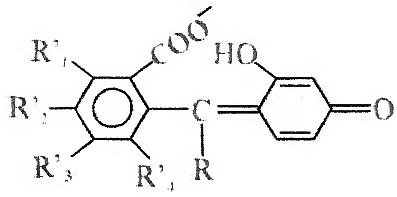
Resorcinol Phthal-as-ein
LVI



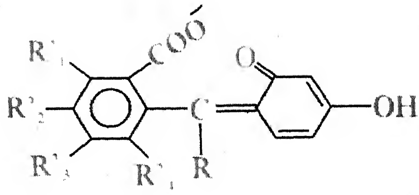
LVII



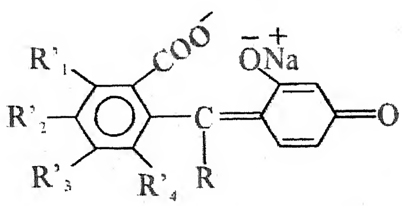
LVIII



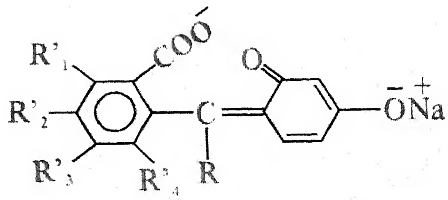
LVII a



LVIII a



LVII b



LVIII b

the two values are in good agreement. In the case of succi-as-eins conjugation does not extend beyond the chiral carbon atom at position 6, (like fuschone structure XXII and its λ_{max} is 390 nm.) as shown in structure (LXI) where resonance occurs only in ring B and this ring possesses benzenoid as well as quinonoid forms where no formal charge is found in the resonating forms, as the charge present in the carboxylate is insulated.

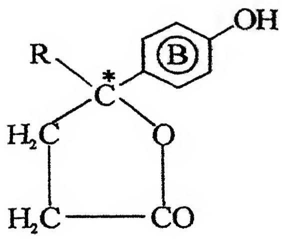
The λ_{max} values of various aryl resorcinol succi-as –eins fall in the range of aryl resorcinol phthal-as-eins (480 nm and in alkali 500 nm) which is explained well when the resonating structures (LXII to LXVI are considered. These structure LXII to LXVI explain the colour of the dyes even in the solid state as due to the formation of ionic structure LXV and LXVI in alkaline medium, a bathchromic shift (500-480- = 20 nm) is observed.

In the case o- quinonoid structures LXIV and LXVI make more contribution than the p – quinonoid structures LXIII and LXV. Due to auxocromic effect of the OH group situated meta to quinonoid oxygen λ_{max} value is found in the range of the phthal-as-eins.

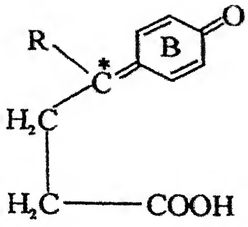
It may be well concluded from the foregoing discussion that no single theory of the colour of the dyes is capable of explaining and predicting the colour with a fair degree if accuracy. However, inspite of this almost sweeping observation, FEMO gas model has been found a better fit than the other theories. There might arise a few mathematical complexities in the application of the two-dimensional free electron gas model. As far as rigrous assumptions are concerned, all the theories, VB, MO and FEMO require these without which it would be impossible to make any calculation even for very simple molecules.

COLOUR (CALCULATION OF ABSOPRTION MAXIMA) OF PHTHAL-AS-EIN DYES:

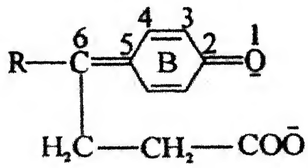
The theoretical values of absorption maxima of phenol phthal-as-eins may only be calculated by making rigorous approximation for the π- electron gas model (equation 8, chapter I). Here each dye molecule is unsymmetrical; hence two equivalent extreme structures with formal charge like phenolphthalein or fluorescein are not possible. Thus, unsymmetrical extended conjugated chains with formal charge at one end only may be present in all the resonating forms, contributing to the dye molecule. Therefore, for calculation purposes major contributing structures LI and LVIIa are considered. Here in all ten electrons are required to take part in the formation of π- electron gas, eight π electrons of four π bonds and two π electrons from the charge free Ol (neutral oxygen atom). The



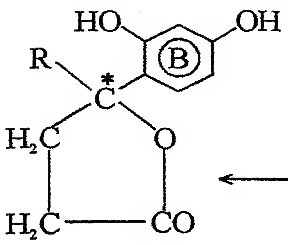
LIX



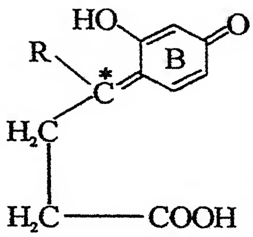
LX



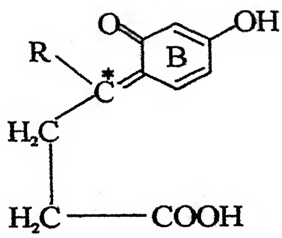
LXI



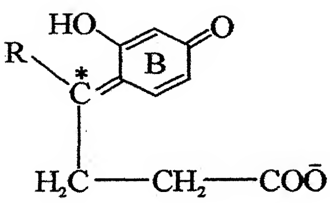
LXII



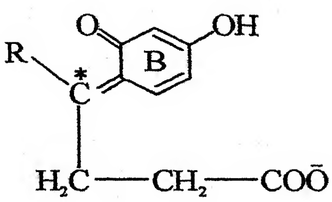
LXIII



LXIV



LXV



LXVI

effective conjugated chains have been depicted by dotted lines and for simplification, the lower portion is neglected by making approximations that do not vitiate the results. Thus, a polar five π electron gas is possible which is responsible for the creation of Coulomb force along the polar molecule with formal charge. To consider the stretching beyond the two ends of the conjugated chain, here it is possible only at one end i.e. at Ol. The value $\alpha = 0.33$ has been derived from the observed λ_{max} value of benzaurine dye XXV depicted in the first chapter with oxygen end groups. Thus by applying the equation 8.

$\lambda_{max} = 127\ (m + \alpha/2)^2\ (m + 3/2)$ in nm

$= 127\ (5 + 0.33/2)^2\ /(5\ + 3/2)$ nm

$= 127\ (5.165)^2\ /6.5$ nm

$= 520$ nm

The value may be regarded as in agreement with the observed value of phenol phthal-as-eins (530-560 nm) and resorcinol phthal-as-eins (530-560 nm). It has not been possible to apply the free electron molecular orbital treatment in the cases of polyhydroxy phenol phthal-as-eins due to unmanageable difficulties presented by their structural complications to derive a simplified expression for the calculation of their absorption maxima.

H.Kuhn[3-4] has more given a refined treatment on the basis of 'one dimensional wave shape potential model' which is applicable for completely symmetrical type of dye molecules. A still better treatment on the basis of 'two dimensional electron gas model' has been proposed by the same author[5] and it is claimed that this may be applied to dye molecules of any complicated shape. However, the prospect of mathematical calculations is very discouraging. The various phenol phthal-as-eins prepared i.e. 2, 4 dimethyl phenyl, phenol phthal-as-ein, 3 carbmethoxy 4 hydroxy phenyl phenol phthal-as-ein, 5 chloro 2 chloromethyl phenyl phenol phthal-as-ein and 3 acenaphthyl phenol phthal-as-ein, are orange, light brown and grey respectively in colour. The bathochromic sift is quite significant in these phenol phthal-as-eins in the alkaline medium. Their λ_{max} values in neutral and in alkaline mediums are 520-545, 510-530, 500-520 and 520-550 nm respectively.

The colours and the λ_{max} values of the dyes,2,4,di methyl phenyl phenol tetra chloro phthal-as-ein, 3- carbmethoxy 4-hydroxy phenyl phenol tetra chloro

phthal-as-eins, 5-chloro 2-chloromethyl phenyl phenol tetra chloro phthal-as-ein,3-acenaphthyl phenol tetra chloro phthal-as-ein; 2,4,dimethyl phenyl phenol nitro phthal-as-ein, 3-carbmethoxy 4-hydroxy phenyl phenol nitro phthal-as-ein, 5-chloro 2- chloro methyl phenyl phenol nitro phthal-as-ein,3-acenaphthyl phenol nitro phthal as-ein are pink(λ_{max} 530-535 nm), orange (λ_{max} 520-530 nm), light brown (λ_{max} -530 nm), light brown (λ_{max} 500-530 nm),light red (λ_{max} -520nm), pinkish (λ_{max} 510-530 nm), light brown (λ_{max} -535 nm) and light brown (λ_{max} 510-530 nm) respectively. These dyes are colourless in the neutral medium and in basic medium give violet, reddish orange with green fluorescence, light violet, violet, pink and pinkish red colours respectively.

The above λ_{max} values observed are in good agreement with the λ_{max} values found for analogous phenol phthal-as-eins.

1. Phenol phthal-as-eins, λ_{max}, 550 nm in alkaline medium.

2. Phenol tetra chloro phthaleins, λ_{max}, 580 nm in alkaline medium.

3. Phenol nitro phthaleins, λ_{max}, 560 nm in alkaline medium.

The higher λ_{max} values observed in the case of some phenol tetra chloro phthal-as-eins and phenol nitro phthal-as-eins may be attributed to the presence of auxochromes in the phenyl ring. These groups may be responsible for the enhancement of colour. Nitro group in the acid part in phenol nitro phthaleins and chlorine atoms in the phenol tetra chloro phthaleins may be partly responsible for the enhancement of λ_{max} values and the colour of the dyes.

In various resorcinol phthal-as-ein dyes prepared the λ_{max} (460-480nm in neutral and 490-520 nm in the alkaline medium) is lower than the λ_{max} values observed in various phenol phthal-as-ein dyes prepared during the present investigations. A possible explanation for this observation may be that in resorcinol phthal-as-ein dyes LVI, there are two hydroxy groups at 2:4 positions instead of one hydroxy group at 4 position as in phenol phthal-as-ein dye structure XLVI. Thus, in one of the main contributing structures of the molecule, conjugation is blocked beyond the 2 hydroxy group LVIIa and consequently, the length of the conjugated chain is decreased. This shortening of the conjugated chain (LVIIIa) may be held responsible for the lowering of the λ_{max} values in these compounds.

All the resorcinol phthal-as-eins studied have absorption maxima at 460-

480 nm in neutral medium, and 490-520 nm in moderate alkaline medium. Value of absorption maxima for these resorcinol phthal-as-ein dyes have been presented in a tabular form at the end of this thesis.

In the case of novel analogues of succineins, the λ_{max} values have been observed for the resorcinol dyes.

2,4 dimethyl phenyl resorcinol succin-as-ein, 3- carbmethoxy 4- hydroxy phenyl resorcinol succin-as-ein. 5-chloro 2-chloromethyl phenyl resorcinol succin-as-ein and 3- acenaphthyl resorcinol succin-as-ein were prepared. The colour of the dyes and their λ_{max} values are dark brown (λ_{max} 460-500 nm), reddish black (λ_{max} 455-500 nm), light brown (λ_{max} 455-510 nm) and brown (λ_{max} 470-500 nm) respectively. These λ_{max} values are in good agreement with the reported arylated succin-as-eins.

1. The significant difference between the phthalein dyes (pyronine dyes) and phthal-as-ein dyes reported in the present dissertation may be observed that while considering the different charged structure to explain their respective colour or to calculate the theoretical value of, in the first case the acid part is not considered at all while in the second case the acid part is involved and is capable of producing a number of charged structures which may be held responsible for their colour.

2. Practically, there is no significant effect of different substituents in the aromatic ring of the acid part but it may be noted that the phthal-as-ein dyes derived from γ -keto acids having 2, 4 dimethyl phenyl, 3- carbmethoxy 4-hydroxy phenyl, 5-chloro 2-chloromethyl phenyl and 3- acenaphthyl subsutituted in the lactol carbon (central carbon atom) show a little more bathochromic shift. As already explained it might be due to these very substituents mentioned above.

3. The distinguishing feature of the two types of dyes (phthal-as-ein XLVa and succin-as-ein XLVb) is that the structure XLVa contains phthalide (aromatic lactone system) whereas structure LXVb contains butyro lactone system. When the quinonoid forms of the two class of dyes i.e. LI and LXI are compared, it is observed that in the case of phthal-as-ein (structure LI), the conjugation is extended between oxygen atom present in ring (B) at position 1 to 8 of the ring (C) beyond the chiral carbon atom present at position 6, which is not possible in the case of succin-as-eins (structure LXI), even then λ_{max} values of two classes of dyes fall within the same region. The high value for λ_{max} for succin-as-eins has already been explained that the ortho quinonoid form makes much more contribution than the para quinonoid form and the auxochromic effect enabled the structure to show λ_{max} value in the range of phthal-as-eins.

4. Though no one single theory is able to explain and predict the colour and the absorption maxima of all types of dyes, still the FEMO gas theory is the best at present to calculate and predict the colour and absorption maxima after making some assumptions which do not vitiate our problem at all. In the present work, the FEMO gas model has been successfully employed and the calculated values are in excellent agreement with the observed.

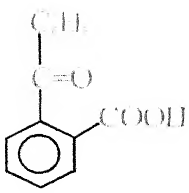
CHEMICAL CONSTITUTION OF PHTHA-AS-EIN DYES:

The open chain substituted or unsubstituted γ -keto acids possess a characteristic structural requirement due to which they are capable of existing in cyclic tautomeric form too. The formation of the ring tautomer (lactol form[6]) takes place due to electrophilic ring chain tautomerism where the electrophile is the proton (hydrogen). Amount of lactol depends on the extent of prototropic change. Generally it has been observed that the γ -keto acids exist chiefly as lactol or equilibrium mixture of ring and chain tautomers[7, 8] . The lactols give well-defined crystalline acetyl derivatives, still retaining their cyclic structures. Therefore, it is obvious that the cyclic tautomer is comparatively more stable form than the chain isomer[9-12] . The formation of pseudoesters[13] of o-benzoyl benzoic acid LXVII has been proposed on the basis of cyclisation of lactol LXVIII that can yield a pseudochloride[14] LXIX. This pseudochloride on heating with appropriate alcohol yields the corresponding ester LXX.

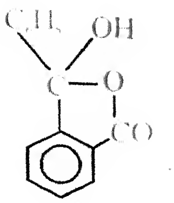
Formation of compound LXXI from o-benzoyl benzoic acid and metaxylene catalyzed by perchloric acid has been proposed through the 3-phenyl phthalyl carbonium ion, where the precursor of this carbonium ion is definitely the cyclic isomer[15,16] LXVIII of 0-benzoyl benzoic acid.

The formation of lactol intermediate has also been used to explain some of the other chemical reactions of o-benzoyl benzoic acid e.g. the reductive coupling[17] of the acid with phosphorous and hydroiodic acid. The cyclic structures for psedoesters have been confirmed by IR[18] and Raman[19] spectra.

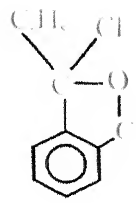
O-acetyl benzoic acid has been shown to yield the aceyl derivative through the formation of lactol[9] intermediate as in the case of o-benzoyl benzoic acid. Peculiarly enough ,o-acetyl benzoyl chloride chemically behaves abnormally. All attempts fail to convert o-acetyl benzoyl chloride into o-acetyl benzaldehyde by Rosenmund reduction or into o-diacetyl benzene[20] . Its conversion to amides with amines has also resulted in failure or very poor yield[21] . This abnormal chemical



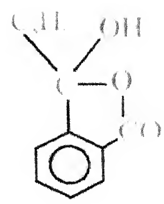
LXVII



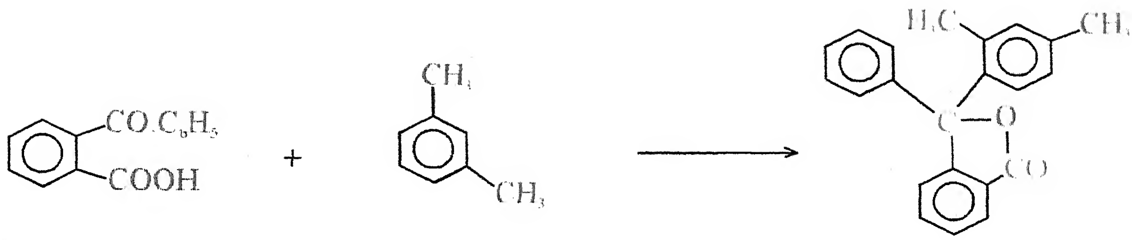
LXVIII



LXIX

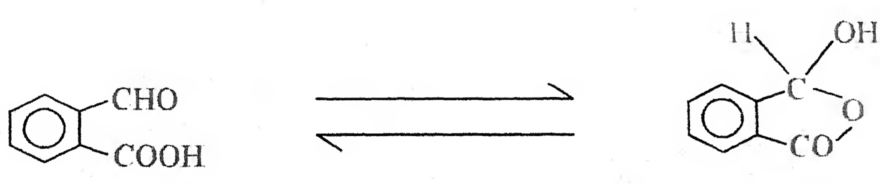


LXX



LXVII

LXXI



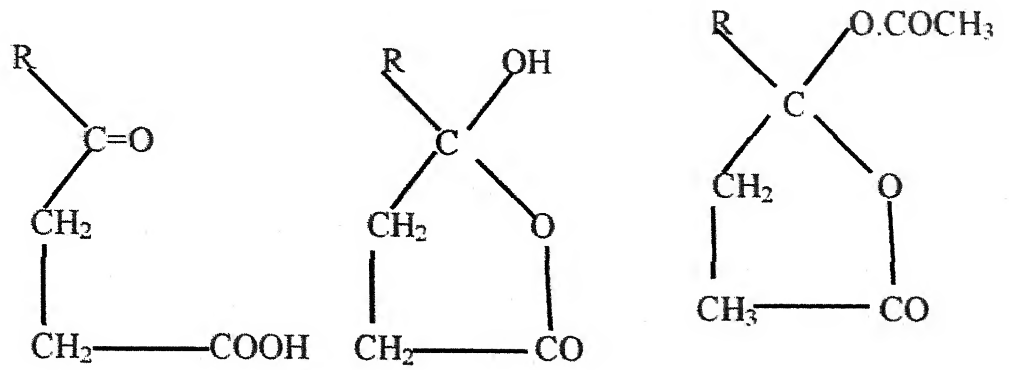
LXXII

LXXIII

behaviour of o-acetyl benzoyl chloride is actually to be expected, if one considers that acid chloride prepared in each case with thionyl chloride, is undoubtedly cyclic and ring tautomeric acid chlorides invariably lead to cyclic products rather than those intended in the above preparative attempts. The lactol formation has been further confirmed by IR[22] and NMR[23] spectral studies. Recently, it has been reported that the acid in liquid form exists chiefly in the lactol form[24].

The formation of pseudoesters as well as a large number of other alkyl derivatives[25,26] of phthal aldehydic acid LXXII can be explained by considering the lactol LXXIII form of the acid. NMR spectra of phthaldehydic acid and o-acetyl benzoic acid indicate that the acids exist in cyclic forms[27]. IR spectrum of phthal aldehydic acid shows bands at 3322 cm^{-1} , 1745 cm^{-1} which support the presence of the acid chiefly in the lactol form.

Open chain γ -keto acids viz. Laevulinic acid or β -acetyl propionic acid (LXXIV, R=CH_3) and β-benzoyl propionic acid (LXXIV, R=C_6H_5) have also been reported to exist in their tautomeric lactol forms LXXV.



LXXIV LXXV LXXVI

These two γ-keto acids form acetyl derivatices[12, 13] LXXVI that is possible through their lactol form only. Due to this type of chemical behaviour, laevulinic acid has been shown to be mixture of ring and chain tautomeris[7, 8.] It has been noted that ring tautomerism[27] is further exalted by changing R to larger alkyl group or aryl group and it further increases when hydrogen atoms on α -carbon atom to the carboxylic group, are also changed to larger alkyl group $\alpha-\beta$-ethylenic bond[28]. Invariably the cyclic isomer has been found to predominate in solution.

SPECTRAL STUDIES OF γ-KETO ACIDS AND THEIR ACETYL DERIVATIVES:

Sixteen γ-keto acids listed earlier in the chapter in four different series i.e. A.B.C. and D have been used for preparation of dyes described in the presentation. IR spectral examination of these acids clearly reveals their existence as a mixture of ring and chain tautomers. There are notable peaks showing the presene of diaryl ketoic >C=O (1675-1700 cm^{-1}); and aryl ketonic group $-CH_2$ - CO-Ar (1660-1670 cm^{-1}); carboxyl>C=O (1695-1710 cm^{-1}); and lactonic >C=O (1735-1790 cm^{-1}); carboxylic –OH (2600-2700 cm^{-1}) and lactol –OH (3100-3500 cm^{-1}).

IR spectra of acetyl derivatives of the acids were also studied. It showed notable peaks of >C = O in acetate (new peaks 1000-1250 cm^{-1} and 1735-1760 cm^{-1}); and lactonic >C = O(1735-1790 cm^{-1}). The peaks due to diaryl Ketonic >C=O (1675-1700 cm^{-1}); aryl ketonic >C = O (1660-1670^{-1});carboxylic >C = O (1695-1710 cm^{-1}) carboxylic – OH (2600-2700 cm^{-1})and lactol –OH (3100-3500 cm^{-1}), which were present originally in acids found absent in the acetyl derivatives of the acids.

NMR SPECTRA OF γ-KETO ACIDS (1-16) AND THEIR ACETYL DERVATIVES:

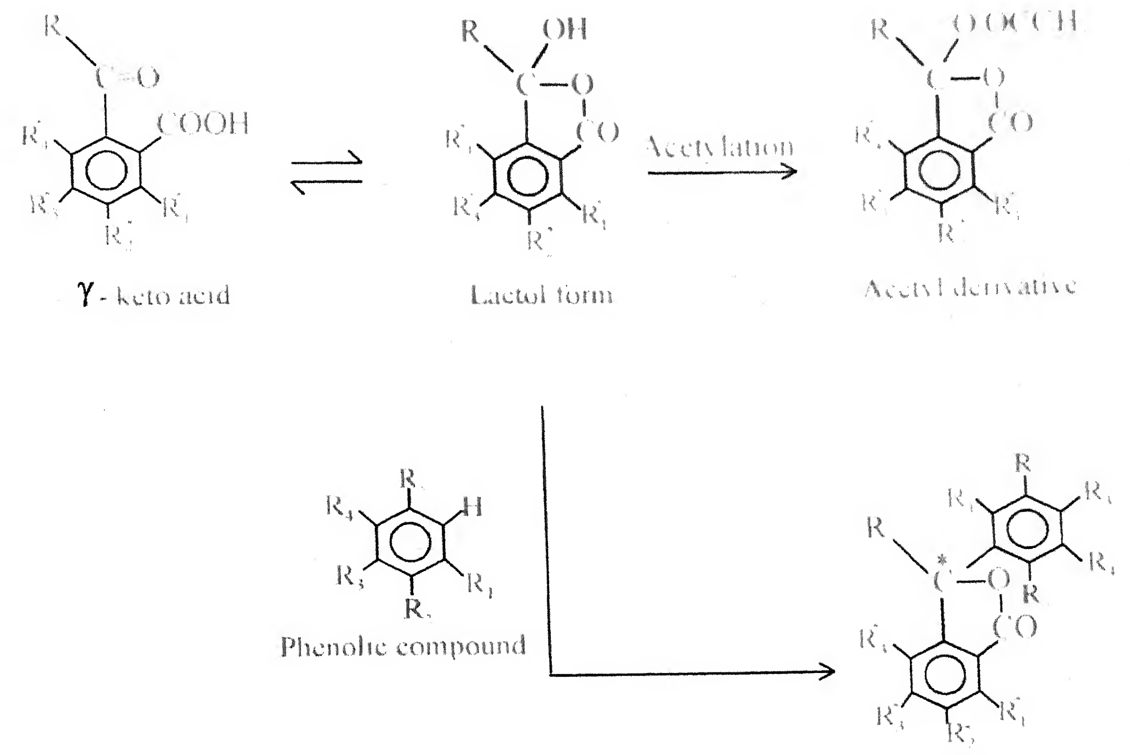
Chemical shifts recorded in NMR spectra of different acids (1-16) and their derivatives further confirm the presence of lactol tautomer in each case (τ=4.2 -4.35) which disappears in the case of their acetyl derivatives and a new chemical shift of O-$COCH_3$ (τ=7.65-7.85) was observed. Thus, it is amply clear that the γ-keto acids exist in keto as well as lactol form which means it is possible to condense these acids with different phenolic compounds giving unsymmetrical phthaleins and succineins. In addition to the above characteristic chemical shifts, others were mostly of aromatic protons (τ=1.85-3.45) depending on the chemical environment in the aromatic rings. However, chemical shift of -COOH in the keto form could not be recorded as NMR spectra were recorded on Varian A-60.

Thus, from the IR and NMR spectral studies of acid and their acetyl derivatives, it is quite clear that γ-keto acids exhibit the phenomenon of ring chain tautomerism and most of their chemical reactions take place via more stable lactol (ring) form. Now it is quite certain that the cyclisation of γ-keto acids provides a hydroxyl group in the form of the corresponding lactol, which is

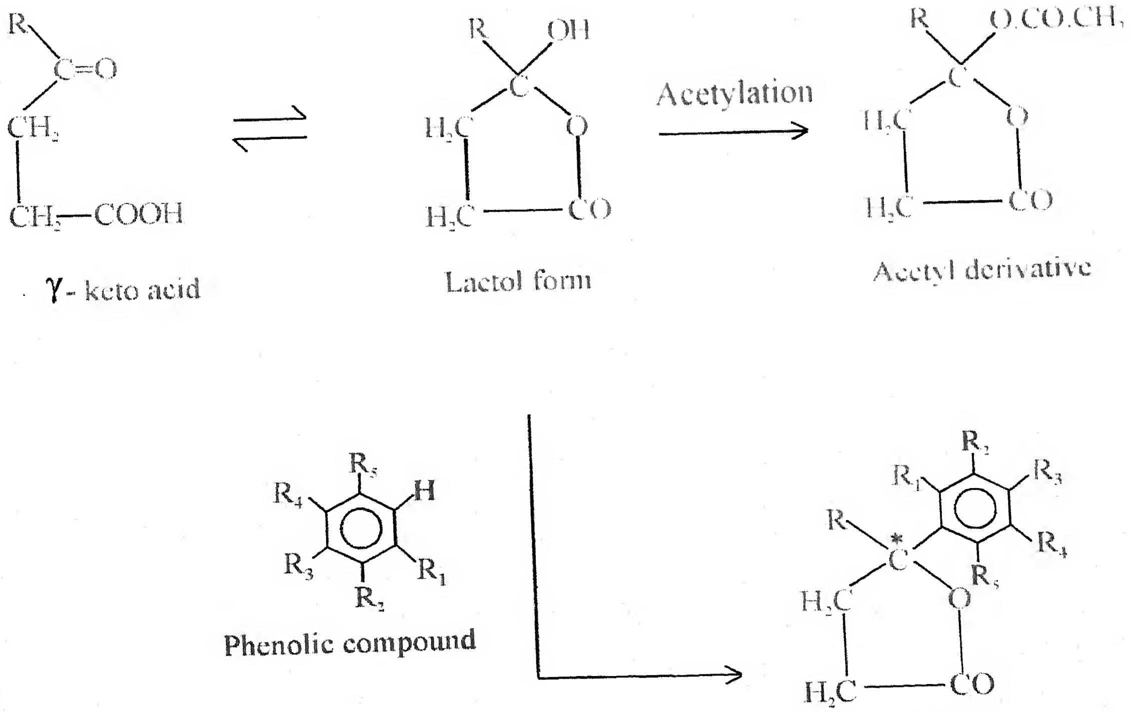
capable of condensing with various aromatic hydroxyl compounds resulting in the formation of the novel analogues of phthaleins, (phthal-as-eins) and succinies (succin-as-eins). It is also quite reasonable to conclude that the acetylation of γ-keto acids takes place via the ring tautomer (lactol form), and also that acetyl derivatives of the acids, phthal-as-a-eins and succin-as-eins possess cyclic structures.

Thus, the formation of acetyl derivatives, phthal-as-eins and succin-as-eins may be shown in the form depicted on the next page.

Recently, Gupta, Beg, Ali and coworkers[29-48] have reported the preparation of a large number of mixed phthal-as eins and succin-as-eins from γ-keto acids. They have also shown that the lactol form of γ-keto acids is involved in the syntheses of these compounds.



XLVa
Phthal-as-ein



XLVb
Succin-as-ein

PART- B

CHEMICAL STRUCTURE OF PHTHAL-AS- EINS AND SUCCIN-AS EINS DYES:

Here, an attempt has been made to assign suitable and satisfactory chemical structure to various novel analogues of phthaleins (phthal-as-ein and succcin-as-eins) incorporated in the thesis on the basis of their chemical behaviour and the study of IR and NMR spectra of γ-keto acids used for the syntheses of phthal-as-eins and succin-as-eins. In order to establish the chemical structure; following sixteen representative dyes have chosen:

A.1.3	(2, 4 dimethyl phenyl) resorcinol phthal-as-ein
B.1.3	(2,4 dimethyl phenyl) resorcinol tetra chloro phtha-as-ein
C.1.3	(2,4 dimethyl phenyl) resorcinol nitro phthal-as-ein
D.1.3	(2,4 dimethyl phenyl) resorcinol succin-as-ein
A.2.3	(3- carbmethoxy 4- hydroxyl phenyl) resorcinol phthal-as-ein
B.2.3	(3-carbmethoxy 4- hydroxyl phenyl) resorcinol tetra chloro phthal-as-ein
C.2.3	(3- carbmethoxy 4- hydroxyl phenyl) resorcinol nitro phthal-as-ein
D.2.3	(3- carbmethoxy 4- hydroxyl phenyl) resorcinol succin-as-ein
A.3.3	(5- chloro 2-chloromethyl phenyl) resorcinol phthal-as-ein
B.3.3	(5- chloro 2-chloromethyl phenyl) resorcinol tetra chloro phthal-as-ein
C.3.3	(5- chloro 2-chloromethyl phenyl) resorcinol nitro phthal-as-ein
D.3.3	(5- chloro 2-chloromethyl phenyl) resorcinol succin-as-ein
A.4.3	(3-acenaphthyl) resorcinol phthal-as-ein
B.4.3	(3-acenaphthyl) resorcinol tetra chloro phthal-as-ein

C.4.3 (3-acenaphthyl) resorcinol nitro phthal-as-ein

D.4.3 (3-acenaphthyl) resorcinol succin-as-ein

For each dye a suitable molecular structure has been suggested on the basis of its elemental analysis, molecular weight determination, identification and determination of the number of the characteristic functional groups. Study of brominated product and determination of number of bromine atoms in each case has been used to find out the number of resorcinol molecules in a dye. Each dye has also been subjected to caustic potash treatment that has helped in assigning the structure of the dye on a firmer basis.

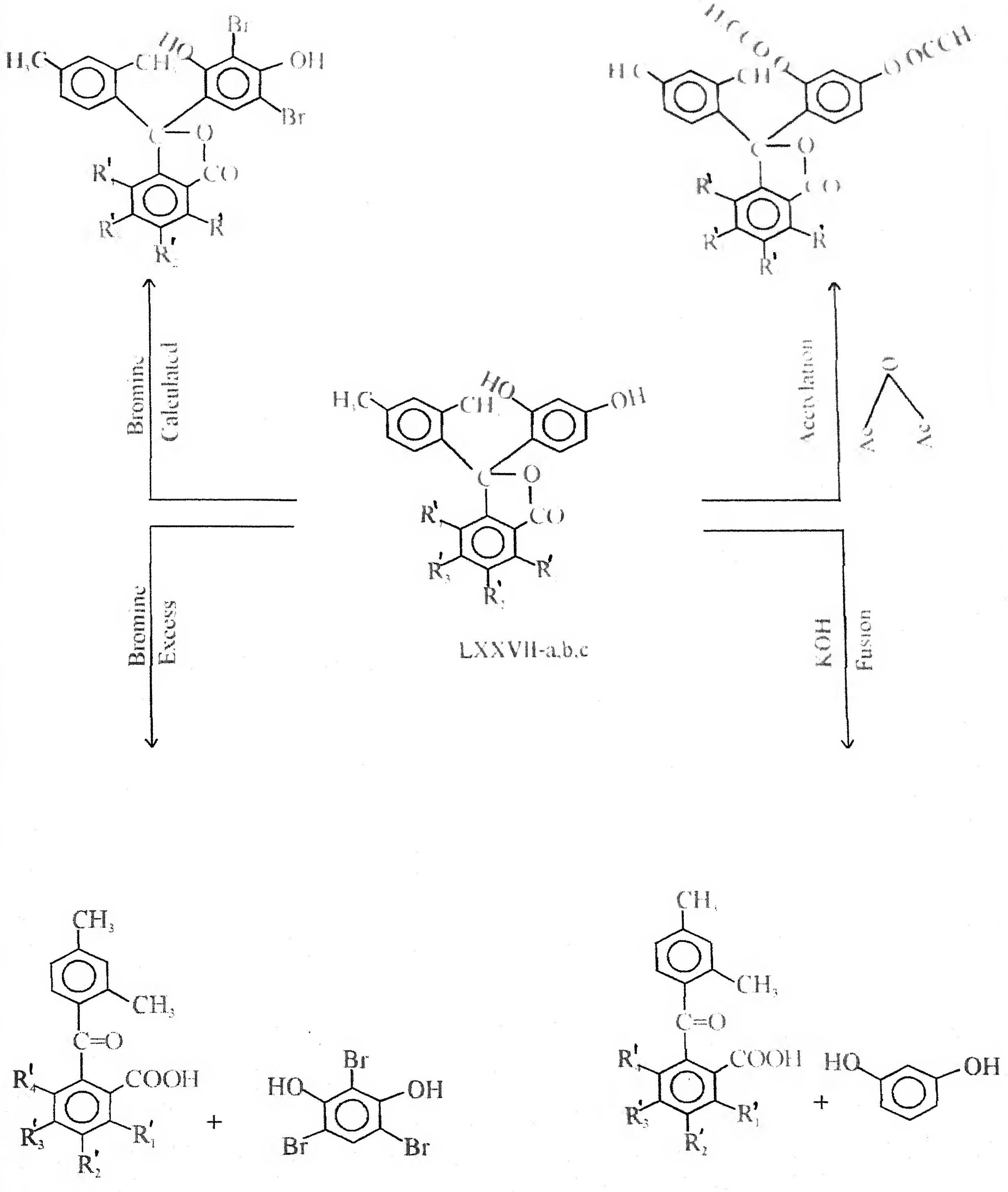
Their IR spectra and also that of their acetyl derivatives have further supported the structures of dyes chosen. Each dyes shows peak due to lactonic>C=O (1735-1790 cm-1) and the phenolic hydroxyl group (3300-3500-cm-1). The peak due the hydroxyl group does not appear in the IR spectra of the acetyl derivatives. New ester peaks were observed in the range of 1000-1250 cm-1 and 1735-1760 cm-1 in the spectra of these acetyl derivatives.

A.1.3 STRUCTURE OF (2, 4 DIMETHYL PHENYL) RESORCINOL PHTHAL-AS-EIN:

The dye was prepared by condensing 2-(2' 4' dimethyl benzoyl) benzoic acid and resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent as described in a subsequent chapter. The dye 2, 4 dimethyl phenyl-resorcinol phthal-as-ein having molecular formula $C_{22}H_{18}O_4$ molecular weight 346 on acetylation yielded a diacetyl derivative indicating the presence of two phenolic groups. When brominated with calculated amount of bromine, the dye gave a dibromo derivative confirming the presence of a molecule of resorcinol in the dye. On caustic potash treatment the dye yielded a molecule of 2-(2' 4' dimethyl benzoyl) benzoic acid and a molecule of resorcinol. With an excess of bromine, the dye yielded a molecule of the same acid and a molecule of tribromo resorcinol. On the basis of chemical evidence, the structure LXXVIIa has been assigned to the dye.

B.1.3 STRUCTURE OF (2, 4 DIMETHYL PHENYL) RESORCINAOL TETRA CHLORO PHTHAL-AS-EIN

The dye (2, 4 dimethyl phenyl) resorcinol tetra chloro phthal-as-ein was prepared by condensing resorcinol and 2-(2' 4' dimethyl benzoyl) tetra chloro benzoic in presence of concentrated sulphuric acid as described later



LXXVIIa $R'_1=R'_2=R'_3=R'_4=H$

LXXVIIb $R'_1=R'_2=R'_3=R_4=Cl$

LXXVIIc $R'_1=R'_2=R'_3=H, R'_4=NO_2$

CHART A

in chapter on the experimental part. The dye having the molecular formula $C_{22} H_{14} Cl_4 O_4$ molecular weight 484, on acetylation yielded a derivative and on bromination too with calculated amount of Br_2 yielded dibromo derivative indicating the presence of two phenolic hydroxyl groups in the dye. Thus only one molecule resorcinol is present in dye molecule. Caustic potash treatment of the dye yielded a molecule of 2-(2' 4' dimethyl benzoyl) tetra chloro benzoic acid and a molecule of resorcinol. On treatment with an excess of bromine the dye molecule gave the same acid with a molecule of tribromo resorcinol. All these reactions can be explained by assigning the structure LXXVIIb to the dye molecule.

C.1.3 STRUCTURE OF (2, 4 DIMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing 2-(2' 4' dimethyl benzoyl)-3-nitro benzoic acid with resorcinol in presence of concentrated supphuric acid as described later in chapter on the experimental part. The dye having the Molecular formula $C_{22} H_{17} NO_6$ molecular weight 391, yielded a diacetyl derivative.of on acetylation and on bromination too with calculated amount bromine, gave a dibromo derivative, indicating the presence of two phenolic hydroxyl groups in the dye molecule. Thus, only one molecule of resorcinol is present in the dye molecule. Caustic potash treatment of the dye yielded a molecule of 2-(2' 4' dimethyl benzoyl)-3-nitro benzoic acid and a molecule of resorcinol. On treatment with excess of bromine, the dye molecule yielded the same acid and a molecule of tribromo resorcinol. From the foregoing reactions the structure LXXVIIc was assigned to (2, 4 dimethyl phenyl) resorcinol nitro phthal-as-ein.

All the reactions of the dyes LXXVIIa, b and c depicted in chart A.

D.1.3 STRUCTURE OF (2, 4 DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:

The dye 2, 4 dimethyl phenyl-resorcinol succin-as-ein having the molecular formula $C_{18}H_{18}O_4$, molecular weight 298 was prepared by condensing β-(2,4 dimethyl benzoyl) propionic acid with resorcinol in presence of concentrated sulphuric acid as described later in chapter on the experimental part. The dye yielded a diacetyl derivative on acetylatiion and a dibromo derivative too on brominatiion with calculated amount of bromine. Caustic potash fusion of the dye gave β-(2, 4 dimethyl benzoyl) propionic acid and a molecule of resorcinol. Treatment of the dye with an excess of bromine yielded β-(2, 4 dimethyl benzoyl) propionic acid and a molecule of tribromo resorcinol. Based on the evidence cited above, the dye has been assigned the structure LXVIId. All the reactions have been depicted in Chart B.

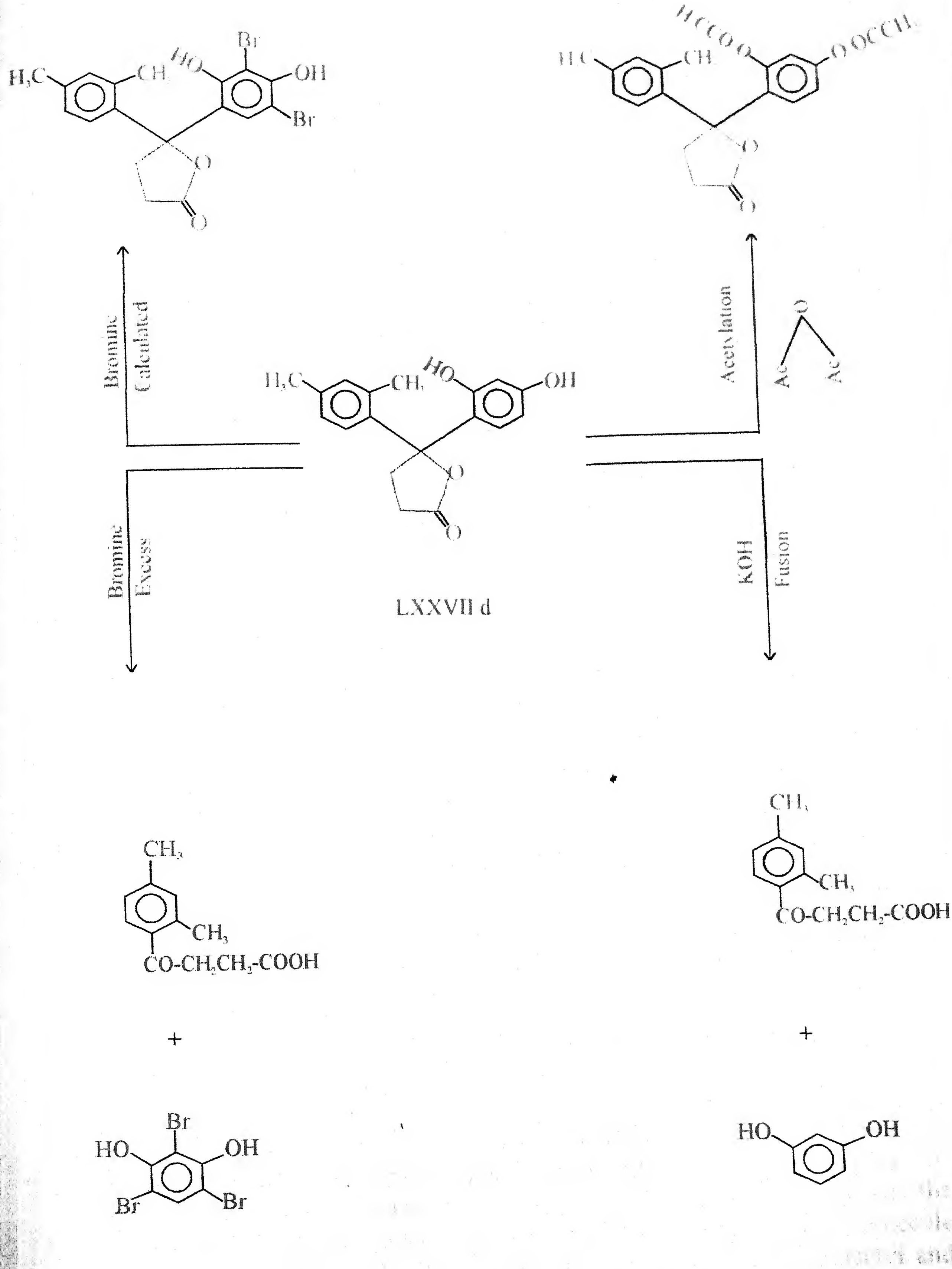

Bromine
Calculated
Bromine
Excess
LXXVII d
Acetylation
KOH
Fusion
CO-CH2CH2-COOH
CO-CH2CH2-COOH

CHART B

A.2.3 STRUCTURE OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCONOL PHTHAL-AS-EIN:

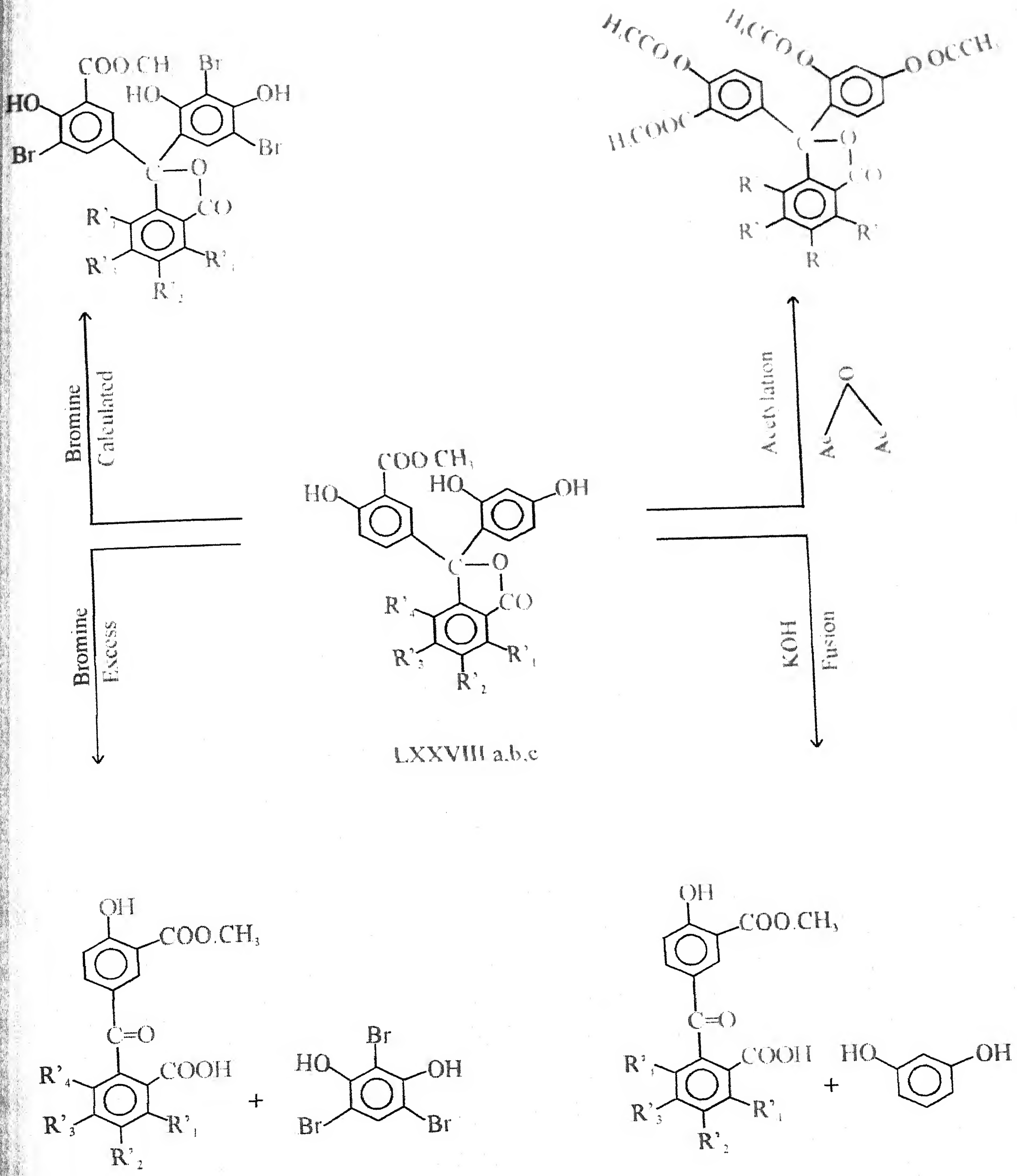
The dye (3 carbmethoxy 4-hydroxy phenyl)-resorcinol-phthal-as-ein having a molecular weight of 380, molecular formula, $C_{21}H_{16}O_7$ was prepared by condensing 2-(3' carbmethoxy 4' hydroxyl benzoyl) benzoic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent as described later in a chapter on experimental part of the work. The dye on acetylation with acetic anhydride in presence of glacial acetic acid yielded a triacetyl derivative and upon bromination with a calucated amount of bromine, yielded a tribromo derivative, thus indicating the presence of one resorcinol molecule in dye molecule. On caustic potash treatment, the dye gave a molecule of 2-(3' carbmethoxy 4' hydroxy benzoyl) benzoic acid and a molecule of resorcinol. The dye, with excess of bromine yielded a molecule of the same acid and a molecule of resorcinol. On the basis of the evidence listed above, the structure LXVIIIa was proposed for the dye

B. 2.3 STRUCTURE OF 3 CARBMETHOXY 4- HYDDROXY PHENYL) RESORCINOL-TETRA CHLORO PHTHAL-AS EIN

The dye 3-carbmethoxy 4-hydroxyl phenyl- resorcinol-tetrachloro phthal-as-ein having molecular formula $C_{21}H_{12}O_7$ molecular weight 518 was prepared by condensing resorcinol and 2-(3' carbmethoxy 4' hydroxyl benzoyl) tetra chloro benzoic acid in presence of a little sulphuric acid as the condensing agent as described later. The dye formed the triacetyl and the tribromo derivatives on acetylatiion and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(3' carbmethoxy 4' hydroxy benzoyl) tetrachloro benzoic acid and a molecule of resorcinol. On treatment with excess of bromine, the dye molecule yielded the same acid and a molecule of tribromo resorcinol. Based on the chemical evidence it could be deduced that the structure of the dye was LXXVIIIb.

C. 2.3 STRUCTURE OF (3- CARBMETHOXY 4- HYDROXY PHENYL) –RESORCINOL – NITRO-PHTHAL –AS -EIN

The dye (3-carbmethoxy 4- hydroxyl phenyl)-resorcinol-nitro-phthal-as-ein was prepared by condensing 2-(3'carbmethoxy 4' hydroxyl benzoyl)-3-nitro benzoic acid in presence of a little concentrated sulphuric acid as the condensing agent as per details given later in the thesis. The dye molecule having the formula C_{21}, H_{15}, NO_9 molecular weight 425, gave triacetyl and tribromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(3'



LXXVIII a $R'_1 = R'_2 = R'_3 = R'_4 = H$

LXXVIII b $R'_1 = R'_2 = R'_3 = R'_4 = Cl$

LXXVIII c $R'_1 = R'_2 = R'_3 = H, R'_4 = NO_2$

CHART C

carbmethoxy 4' hydroxyl benzoyl)-3-nitro benzic acid and a molecule of resorcinol. The dye, with excess of bromine yielded a molecule of the same acid and a molecule of tribromo resorcinol. This evidence clearly established that the structure of the dye is as depicted LXXVIIIc.

The foregoing reactions of the LXXVIIIa, b and c are shown in chart C.

D. 2.3 STRUCTURE OF (3-CARBMETHOXY 4-HYDROXY PHENYL)-RESORCINOL-SUCCIN-AS-EIN

This dye was prepared by condensing resorcinol with β- (3-carbmethoxy 4-hydroxyl benzoyl) propionic acid in presence of some drops of concentreated sulphuric acid as the condensing agent as described later. The dye (3-carbmethoxy 4-hydroxyl phenyl)-resorcinol-succin-as-ein has the molecular weight of 344 molecular formula $C_{18}H_{16}O_7$ on acetylation yielded triaetyl derivative and a tribromo derivative too on bromination with calculated amount of bromine, showing the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded β-)3-carbmethoxy 4-hydroxyl benzoyl) propionic acid and a molecule of resorcinol. On treatment with excess of bromine, the dye molecule yielded the same acid and a molecule of tribromo resorcinol. Based on the chemical evidence it could be deduced that the structure of the dye was LXXVIIId.

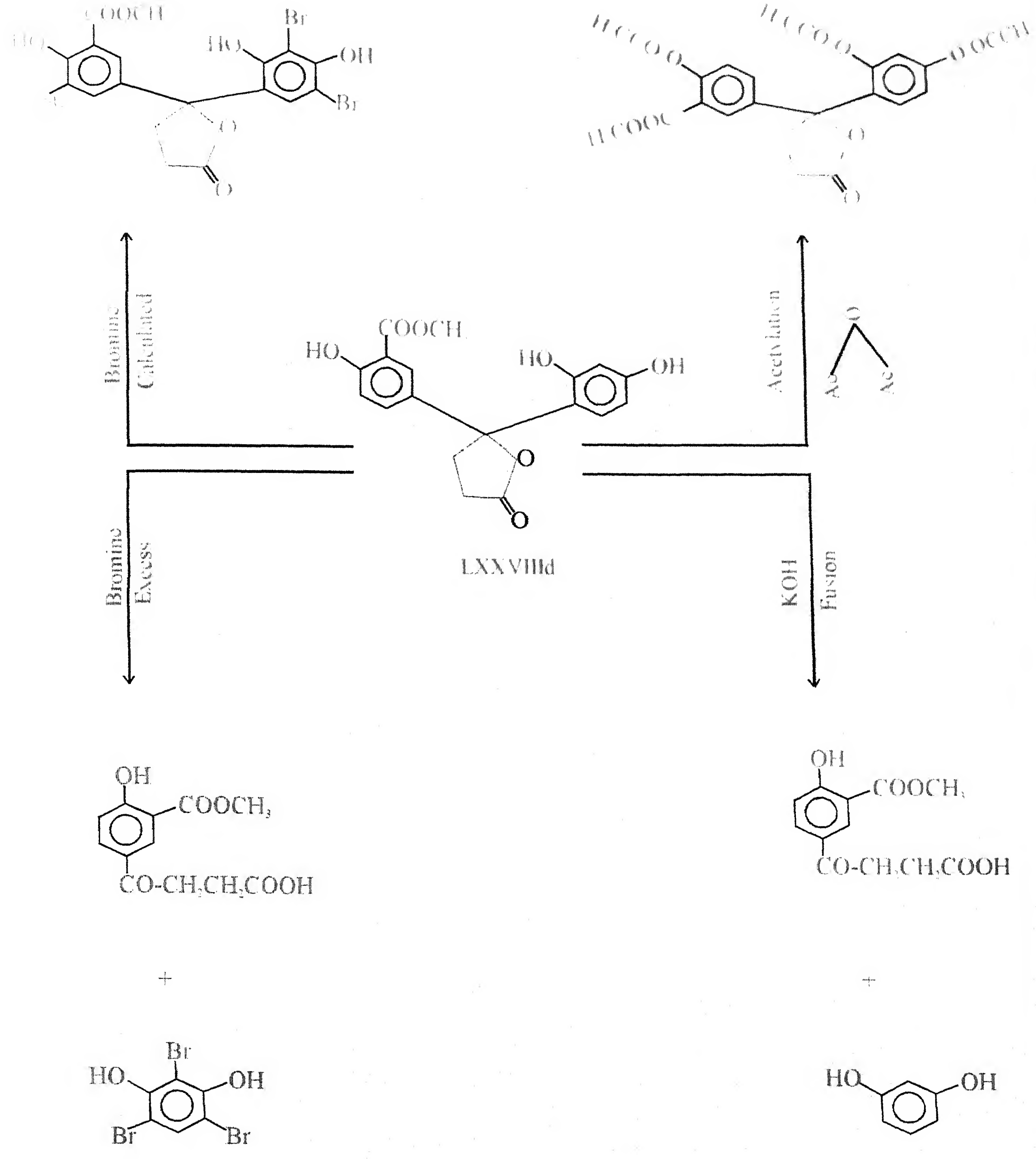
All these reactions have been summarized in chart D.

A.3.3 STRUCTURE OF (5-CHLORO 2-CHLOROMETHYL PHENYL)-RESORCINOL-PHTHAL-AS-EIN:

The dye (5- chloro 2-chloromethyl phenyl)-resorcinol-phthal-as-ein was prepared by condensing 2-(5-chloro 2-chloromethyl benzoyl) benzoic acid with resorcinol in presence of 3-4 drops of concentrated sulphuric acid as described later in the thesis. The dye molecule having the molecular formula $C_{21}H_{14}Cl_2O_4$ molecular weight 401, gave diacetyl and dibromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(5-chloro 2-chloromethyl benzoyl) benzoic acid and a molecule of resorcinol. The dye when treated with an excess of bromine formed 2-(5-chloro 2-chloromethyl benzoyl) benzoic acid and a molecule of tribromo resorcinol. These results lead us to formulate the structure of the dye as LXXIXa.

B.3.3 STRUCTURE OF (5-CHLORO 2-CHLOROMETHYL PHENYL) RESORCINOL TETRA CHLORO PHTHAL-AS-EIN:

The dye (5-chloro 2-chloromethyl phenyl) resorcinol tetra chloro phthal-as-ein was synthesized by the condensation of 2-(5-chloro 2-



COOCH
HO
HO
OH
Bromine
Calculated
Acetylation
Ac
O
Ac
Bromine
Excess
KOH
Fusion
LXXVIIId
OH
COOCH
CO-CH CH COOH
HO
OH
Br
Br
Br

CHART D

chloromethyl benzoyl) tetra chloro benzoic acid with resorcinol in presence of a little concentrated sulphuric acid as per description later in the experimental part. The dye has the molecular weight of 539, molecular formula $C_{21}H_{10}Cl_6O_4$ on acetylation yieldeddiacetyl derivative and a dicromo derivative too on bromination with calculated amount of bromine, showing the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2—(5-chloro 2-chloromethyl benzoyl) tetra chloro benzoic acid and a molecule of resorcinol. On treatment with excess bromine, the dye yielded 2-(5-chloro 2-chloromethyl benzoyl) tetra chloro benzoic acid along with a molecule of tribromo resorcinol. The dye was thus assigned the structure LXXIXb.

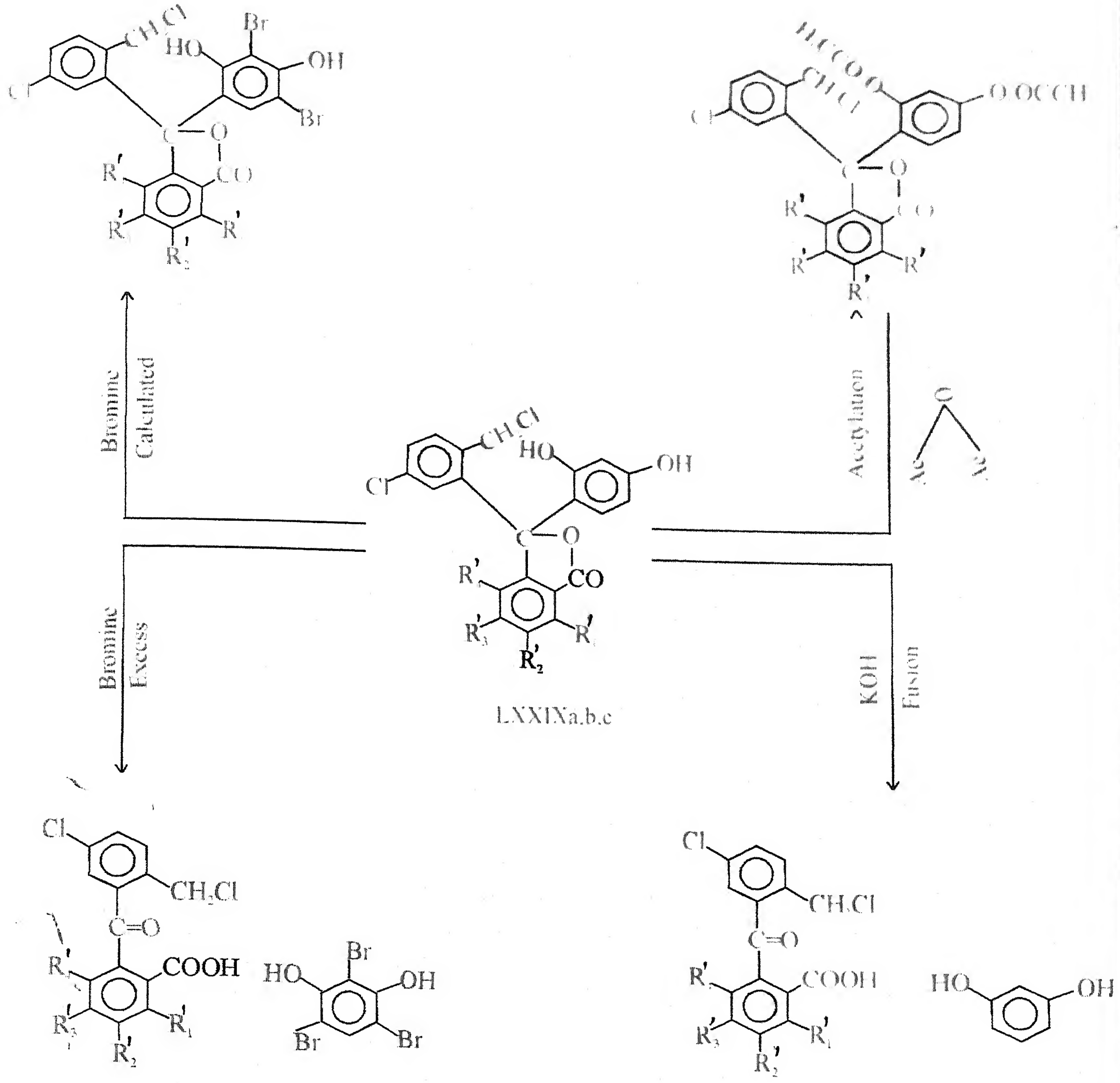
C.3.3 STRUCTURE OF (5- CHLORO 2- CHLOROMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye (5-chloro 2- chloromethyl phenyl) resorcinol nitro-phthal-as-ein, with the molecular weight 446, molecular formula $C_{21}H_{13}NCl_2O_6$, was obtained by condensing resorcinol with 2-(5-chloro 2-chloromethyl benzoyl)-3-nitro benzoic acid in presence of a small amount of sulphuric acid as a condensing agent as per detail listed later. The dye gave diacetyl and dibromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(5-chloro 2-chloromethyl benzoyl)-3-nitro benzoic acid and a molecule of resorcinol. Treatment of the dye with excess of bromine leads to the formation of 2-(5-chloro 2-chloromethyl benzoyl)-3-nitro benzoic acid along with a molecule of tribromo resorcinol. Based on the evidence cited above, the dye molecule was assigned the structure LXXIXc.

All the chemical reactions of the dyes LXXIXa,b and c are summarized in chart E.

D.3.3 STRUCTURE OF (5- CHLORO 2- CHLOROMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:

The dye having molecular formula $C_{17}H_{14}O_4Cl_2$ mol weight 353, was prepared by condensing β-(5-chloro 2-chloromethyl benzoyl) propionic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent as described later in a chapter on experimental part of the work. The dye formed the diacetyl and the dibromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. On caustic potash treatment, the dye gave a molecule of β-(5-chloro 2-chloromethyl benzoyl) propionic acid and a molecule of resorcinol. The dye,



LXXIXa $R'_1 = R'_2 = R'_3 = R'_4 = H$
LXXIXb $R'_1 = R'_2 = R'_3 = R'_4 = Cl$
LXXIXc $R'_1 = R'_2 = R'_3 = H$, $R'_4 = NO_2$

CHART E

with excess of bromine yielded a molecule of the same acid and a molecule of tribromo resorcinol. On the basis of the evidence listed above, the structure LXXIXd was proposed for the dye molecule.

All the reactionsdescribed above have been summarized in chart F.

A.4.3. (3-ACENAPHTHYL) RESORCINOL PHTHAL-AS-EIN:

The dye (3-acenaphthyl)-resorcinol-phthal-as-ein was prepared by condensing resorcinol with 2-(3' acenathoyl) benzoic acid using a small amount of concentrated sulphuric acid as the codensing agent. The dye was found to have a molecular formula $C_{26} H_{18} O_4$ and molecular weight 394. The dye gave diacetyl and dibromo derivatives on acetylation and bromination with calculate amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(3' acenaphthoyl) benzoic acid and a molecule of resorcinol. But the dye on treatment with excess of bromine formed 2-(3' acenaphthoyl) benzoic acid along with a molecule of tribromo resorcinol. The evidence conclusively pointed out the structure LXXXa for the dye.

B.4.3 STUCTURE OF 3-ACENAPHTHYL) RESORCINOL TETRA CHLORO PHTHAL-AS-EIN:

The dye (3' acenaphthyl) resorcinol tetra chloro phthal-as-ein, having the molecular formula $C_{26}H_{14}Cl_4O_4$ and molecular weight 532 was prepared by the condensation of 2-(3'acenaphthoyl) tetra chloro benzoic acid with resorcinol in presence of concentrated sulphuric acid as the condensing agent. The dye formed the diacetyl and dibromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. On caustic potash treatment, the dye yielded 2-(3' acenaphthoyl) tetra chloro benzoic acid and a molecule of resorcinol was formed. The reaction of the dye with an excess of bromine yielded 2-(3' acenaphtoyl) tetrachloro benzoic acid and a molecule of tribromo resorcinol. The dye was assigned the structure LXXXb on the basis of the above evidence.

C.4.3 STRUCTURE OF (3- ACENAPHTHYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye (3 acenaphthyl)-resercinol-nitro-phthal-as-ein has been prepared by condensing 2-(3' acenaphthoyl)-3-nitro benzoic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as described later. The dye with molecular weight 439 and molecular formula $C_{26} H_{17} NO_6$ yielded on acetyylation a diacetyl derivative and a dibromo derivative on bromination with a calculated amount of bromine indicating the presence of a molecule of resorcinol in the bigger dye molecule. Caustic potash

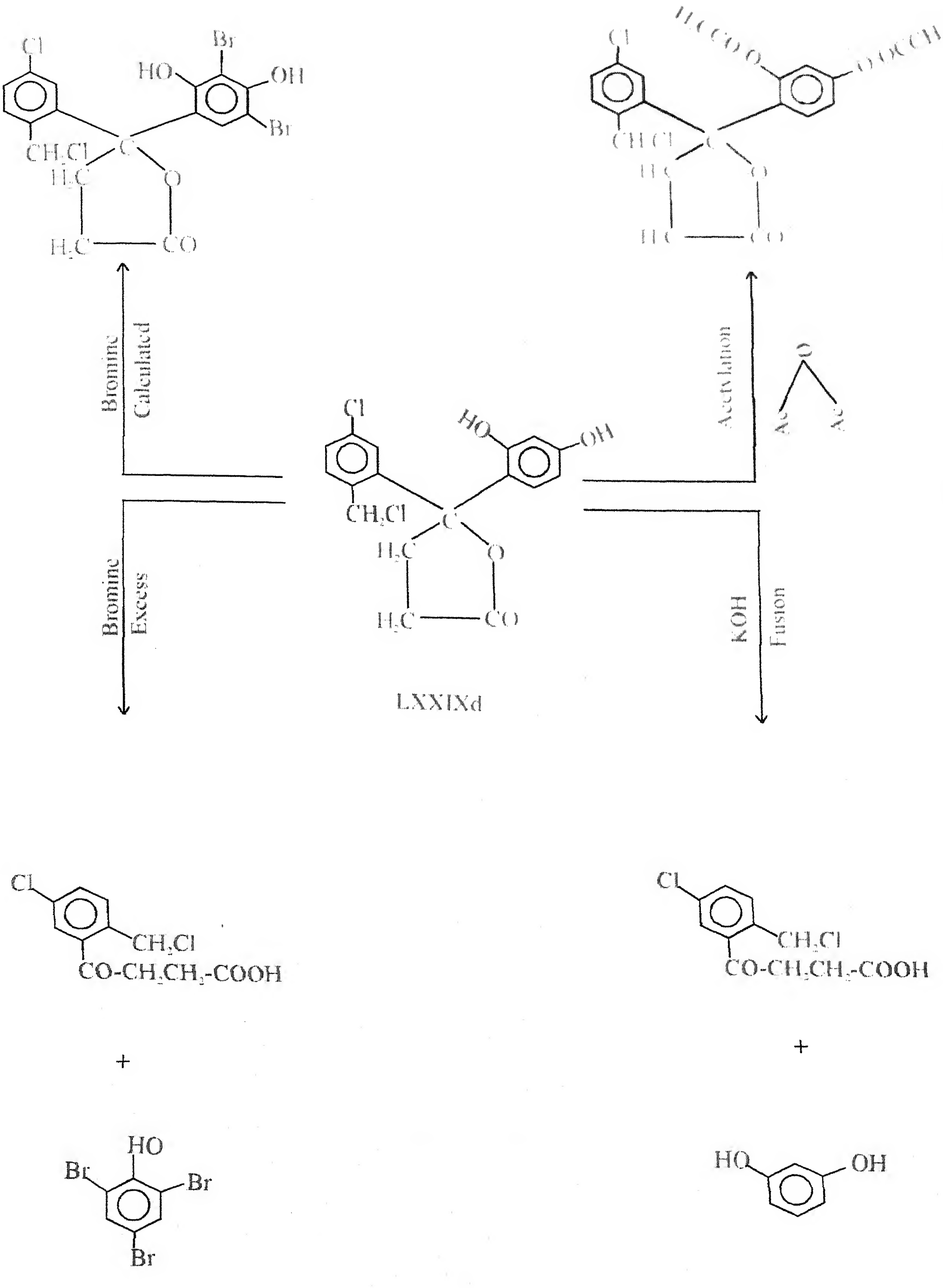
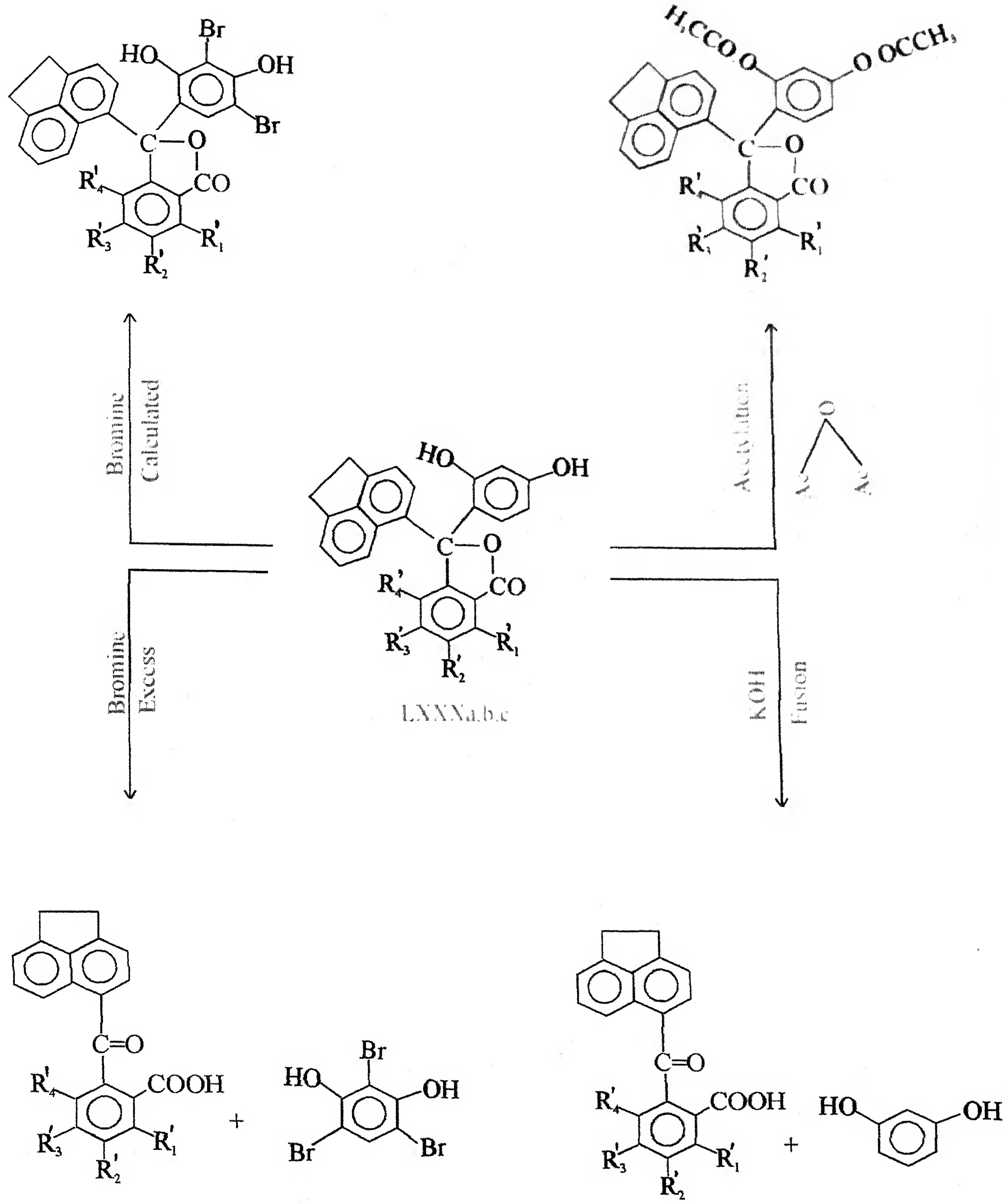

Bromine
Calculated
Acetylation
Bromine
Excess
KOH
Fusion
LXXIXd

CHART F



LXXIXa $R'_1=R'_2=R'_3=R'_4=H$
LXXIXb $R'_1=R'_2=R'_3=R'_4=Cl$
LXXIXc $R'_1=R'_2=R'_3=H, R'_4=NO_2$

CHART G

treatment gave 2-(3' acenaphthoyl)-3-nitro benzoic acid and a molecule of resorcinol. Treatment of the dye with an excess of bromine yielded 2-(3' acenaphthoyl)-3-nitro benzoic along with a molecule of tri bromo resorcinol. On the basis of evidences deduced above the dye was assigned the structure LXXXc.

All the chemical reactionsof the dyes LXXXa, b and a are summarized in chart G.

D.4.3 STRUCTURE OF (3- ACENAPHTHYL) RESORCINOL SUCCIN-AS-EIN:

The dye (3' acenaphthyl) resorcinol succin-as-ein was prepared by condensing β-(3' acenaphthoyl) propionic acid with resorcinol in presence of a little concentrated sulphuric acid as described later. It had the molecular formula C_{22} H_{18} O_4 and molecular weight 346. It yielded on acetylation a diacetyl derivative and a dibromo derivative on bromination with a calculated amount of bromine indicating the presence of a molecule of resorcinol in the bigger dye molecule. Caustic potash treatment of the dye lead to the formation of β-(3' acenaphthoyl) propionic acid along with a molecule of ~~tribromo~~ resorcinol. With excess of Br_2 dye yielded same acid and tribromo resorcinol. The dye was, therefore, assigned the structure LXXXd on the basis of the evidence.

All the reaction of the dye molecule have been graphically outlined in the chart H.

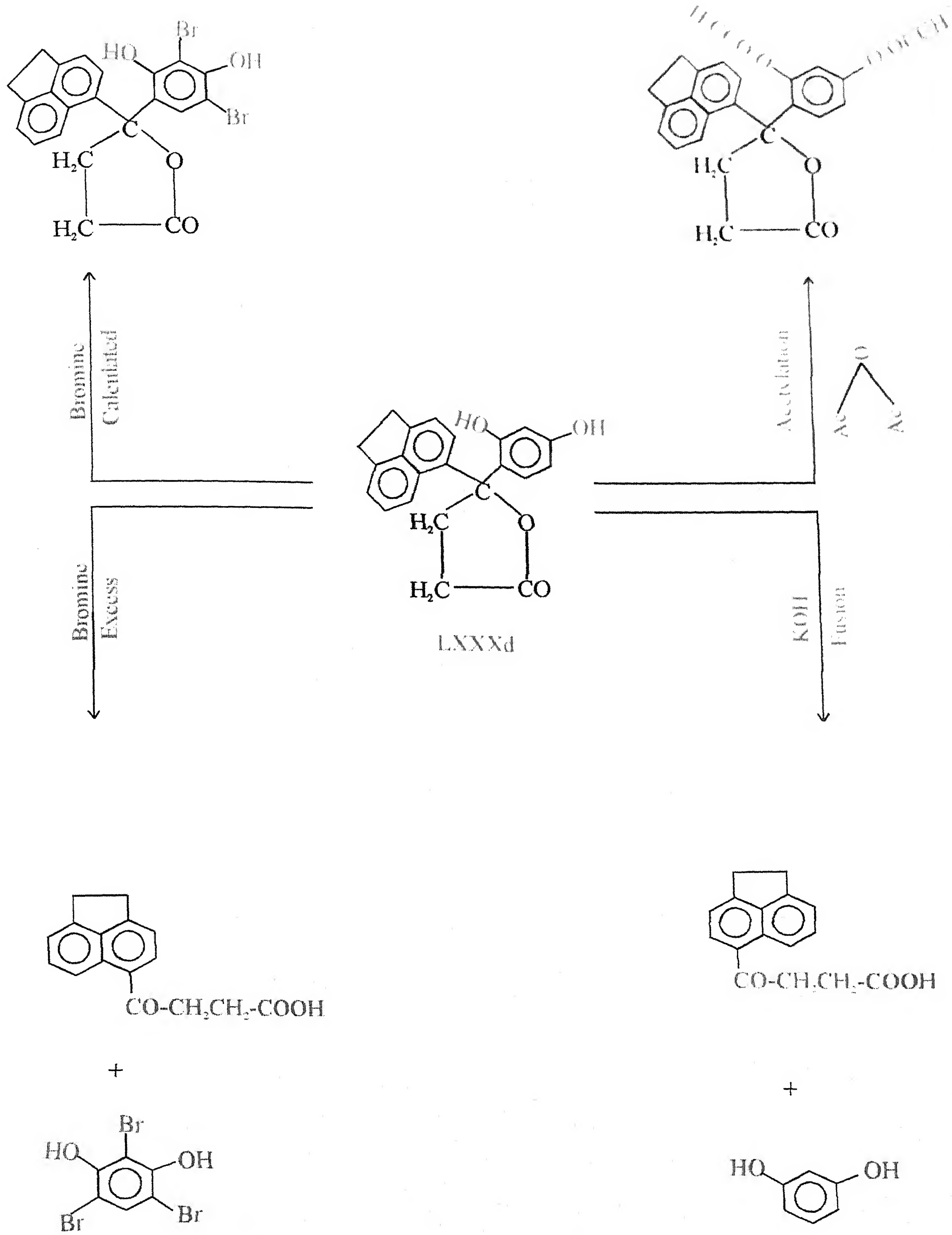

Bromine Calculated
Bromine Excess
Acetylation
KOH Fusion
LXXXd
CO-CH$_2$CH$_2$-COOH
+

CHART H

IR spectra of γ - KETO ACIDS AND THEIR ACETYL DERIVATIVES λ-max (KBr)

	Acid and their Acetyl derivatives	Diaryl ketonic >C=O	Aryl ketonic $-H_2$ C.CO.Ar	Carboxyl >C=O	lactonic >C=O	Carboxyl - OH	Lactol - OH	Ester group	Phenolic - OH
	1	2	3	4	5	6	7	8	9
A.1	2-(2' 4' dimethylbenzoyl) Benzoic acid	1690	-	1710	1735	2665(week)	3660	-	-
	Acetyl derivative	-	-	-	1785	-	-	1750, 1235, 1230,1010.	-
A.2	2-(3' carbmethoxy 4'hydroxy-benzoyl)-benzoic acid	1695	-	1705	1740	2645(week)	3640	-	3560
	Acetyl derivatie	-	-	-	1782	-	-	1760, 1240, 1230, 1035	-
A.3	2-(5' chloro 2' chloromethyl - benzoyl)-benzoic acid	1700	-	1710	1742	2645 (week)	3670	-	-
	Acetyl derivative	-	-	-	1787	-	-	1755, 1250, 1220, 1010	-
A.4	2-(3' acenaphthoyl Benzoic acid	1695	-	1700	1735	2660(week)	3650	-	-
	Acetyl derivative	-	-	-	1780	-	-	1755, 1235, 1210	-
B.1	2-(2' 4' dimethyl benzoyl) Tetrachloro benzoic acid	1700	-	1705	1742	2665(week)	3650	-	-
	Acetyl derivative	-	-	-	1785	-	-	1760, 1250, 1230, 1010.	-

IR spectra of γ - KETO ACIDS AND THEIR ACETYL DERIVATIVES λ-max (KBr)

	Acid and their Acetyl derivatives	Diaryl ketonic >C=O	Aryl ketonic -H_2 C.CO.Ar	Carboxyl >C=O	lactonic >C=O	Carboxyl - OH	Lactol - OH	Ester group	Phenolic - OH
B.2	2-(3' carbmethoxy 4' hydroxy)-trachloro benzoic acid	1685	-	1700	1740	2670(week)	3660	-	3560
	Acetyl derivative	-	-	~~1785~~	1785	-		1755, 1250, 1230, 1010	-
B.3	2-(5'chloro 2' chloromethyl - benzoyl) tetra- chlorobenzoic acid	1675	-	1695	1735	2630 (week)	3290	-	-
	Acetyl derivative	-	-	-	1790	-	-	1745, 1250, 1220,1030	-
B.4	2-(3' acenaphthoyl) tetra- chlorobenzoic acid	1700	-	1710	1735	2660	3120	-	-
	Acetyl derivative	-	-	-	1778	-	-	1745, 1240, 1210,1010	-
C.1	2-(2' 4'dimethylbenzoyl) Nitro benzoic acid	1682	-	1695	1745	2650	3300	-	-
	Acetyl derivative	-	-	-	1785	-	-	1750, 1250, 1220, 1030	-
C.2	2-(3' carbmethoxy 4' hydroxy-benzoyl)-3-Nitro benzoic acid	1680	-	1690	1740	2610	3450	-	3570
	Acetyl derivative	-	-	-	1780	-	-	1740, 1240, 1210, 1010	-
C.3	2-(5' chloro 2' chloromethyl benzoyl)-3-Nitro benzoic acid	- 1700	-	1710	1735	2660	3120	-	-

IR spectra of γ - KETO ACIDS AND THEIR ACETYL DERIVATIVES λ-max (KBr)

	Acid and their Acetyl derivatives	Diaryl ketonic >C=O	Aryl ketonic -H_2 C.CO.Ar	Carboxyl >C=O	lactonic >C=O	Carboxyl - OH	Lactol - OH	Ester group	Phendic - OH
	Acetyl derivative	-	-	-	1778	-	-	1745, 1240, 1210,1010	-
C.4	2-(3' acenaphthoyl) -3-Nitro- benzoic acid	1670	-	1705	1735	2620(week)	3460	-	-
	Acetyl derivative	-	-	-	1785	-	-	1740, 1240, 1210,1005	-
D.1	β-(2- 4 dimethylbenzoyl) propionic acid	1695	1665	1710	1742	2640(week)	3500	-	-
	Acetyl derivative	-	-	-	1778	-	-	1745, 1230, 1205, 1000	-
D.2	β-(3' carbmethoxy 4' hydroxy-benzoyl)- propionic acid	1680	1660	1710	1740	2660(week)	3450	-	3580
	Acetyl derivative	-	-	-	1785	-	-	1745, 1250, 1210, 1010	-
D.3	β-(5' chloro 2' chloromethyl Benzoyl) propionic acid	1700	1668	1705	1742	2655(week)	3500	-	-
	Acetyl derivative	-	-	-	1775	-	-	1755, 1220, 1220, 1005	-
D.4	β-(3- acenaphthoyl) propionic acid	1682	1670	1695	1745	2650	-	-	-
	Acetyl derivative	-	-	-	1785	-	-	1750, 1250, 1220, 1030	-

NMR SPECTRA OF γ-KETO ACIDS AND THEIR ACETYL DERIVATIVES

Acids and their acetyl derivatives	Solvent	Chemical shift (τ)
1	2	3
A.1 2-(2' 4' dimethyl benzoyl) Benzoic acid	DMSO	1.95-3.45(m; 7 unsymmetrical aromatic protons) 7.85(s; 6 two C$\underline{H}_3$ Protons); 4.30 (singlet, lactol-OH proton).
Acetyl derivative	$CDCl_3$	1.90-3.35(m; 7 aromatic protons); 7.80 (s; 6 two C$\underline{H}_3$ protons) 7.65(Singlet 3-OOCC$\underline{H}_3$ protons).
A.2 2-(3' carbmethoxy 4'hydroxy benzoyl) benzoic acid	DCl_3	1.85-3.40 (m; 7 unsymmetrical aromatic protons); 4.32(br; s; Lactol proton); 4.78 (s; 1 phenolic –O$\underline{H}$ proton); 5.90(s; 3-COOC$\underline{H}_3$ protons).
Acetyl derivative	$CDCl_3$	1.80-3.35 (m; 7 unsymmetrical aromatic protons); 7.65 (s; 3 lactol-O.OCC$\underline{H}_3$ Proton); 7.80 (s; phenolic 3- O.OCCH_3 protons); 5.90(s;- 3-COOC$\underline{H}_3$ proton)
A.3 2-(5' chloro 2' chloromethyl benzoyl) benzoic acid	DMSO	1.92-3.20(m; 7 unsymmetrical aromatic protons); 4.35 (br; S; lactol proton) 6.5 (s: 2-C$\underline{H}_2$Cl protons)
Acetyl derivative	DMSO	1.95-3.25(m, 7 unsymmetrical aromatic protons); 7.6$\underline{0}$ (S,3-O.OCC$\underline{H}_3$ protons, 6.5 (s; 2 C$\underline{H}_2$Cl protons)
A.4 2-(3' acenapthoyl) Benzoic acid	DMSO	1.85-2.85 (m; 9 aromatic protons):4.25(br; s; lactol $\underline{H}$); 7.40 (m; 4-C$\underline{H}_2$ - C$\underline{H}_2$ – protons)
Acetyl derivative	$CDCl_3$	1.95- 2.90(m; 9 aromatic protons); 7.65(s, 3-OOCC$\underline{H}_3$ Protons); 7.45 (m; 4-C$\underline{H}_2$-C$\underline{H}_2$-protons)

NMR SPECTRA OF γ-KETO ACIDS AND THEIR ACETYL DERIVATIVES

	Acids and their acetyl derivatives	Solvent	Chemical shift (τ)
B1.	2-(2' 4' dimethyl benzoyl), Tetrachloro benzoic acid	$CDCl_3$	2.30- 3.25(m; 3 symmetrical protons); 4.32(br; S; Lactol 1-O$\underline{H}$ proton; 7.90 (S; 6 two C$\underline{H}_3$ protons).
	Acetyl derivative	$CDCl_3$	2.35-3.20 (m; 3 unsymetrical aromatic protons); 7.60 (S; Lactol 3-O.OCC$\underline{H}_3$ protons) ; 7.82 (S; 6 Two – C$\underline{H}_3$ Protons)
B.2.	2-(3' carbmethoxy 4' hydroxy Benzoyl) tetrachloro benzoic Acid	$CDCl_3$	2.30-3.20 (m; 3 unsymmetrical aromatic protons); 4.30 (S; br; Lactol 1-O$\underline{H}$ proton); 4.78 (S; 1 phenolic O$\underline{H}$ proton); 5.90 (S; 3-COOC$\underline{H}_3$ protons).
	Acetyl derivative	$CDCl_3$	2.35-3.40 (m;3 unsymmetrical aromatic protons); 7.60 (S; Lactol 3-O.OCCH_3 protons); 5.90 (S; 3-COOC$\underline{H}_3$ protons); 7.80 (S; Phenolic 3-OOCC$\underline{H}_3$ protons).
B.3	2-(5'chloro 2' chloromethyl Benzoyl) tetrachloro benzoic Acid	DMSO	1.95-3.25 (m; 3 unsymmetrical aromatic protons); 4.30 (Br; S; Lacto –O$\underline{H}$ proton) ; 6.55 (S; 2-C$\underline{H}_2$-Cl protons)
	Acetyl acid	$CDCl_3$	2.05-3.40 (m; 3 unsymmetrical aromatic protons); 7.60 (S; 3-OOCC$\underline{H}_3$); 6.5 (S; 2-C$\underline{H}_2$-Cl protons).
B.4	2-(3' acenaphthoyl) tetra Chlorobenzoic acid	DMSO	1.95-3.30 (m, 5 aromatic ring H); 4.20 (S; lactol H); 7.40 (m; 4-C$\underline{H}_2$-C$\underline{H}_2$-Protons)
	Acetyl derivative	$CDCl_3$	2.05-3.35 (m; 5 aromatic ring protons); 7.65 (S, 3, O-OC-C$\underline{H}_3$ protons); 7.40 (m; 4-C$\underline{H}_2$-C$\underline{H}_2$- protons).

NMR SPECTRA OF γ-KETO ACIDS AND THEIR ACETYL DERIVATIVES

Acids and their acetyl derivatives		Solvent	Chemical shift (τ)
C.1	2-(2' 4' dimethyl benzoyl) 3-nitro benzoic acid	$CDCl_3$	2.35-3.25 (m; 6 unsymmetrical protons); 4.32 (br, S; lactol –O$\underline{H}$ proton); 7.90 (S; 6 two-C$\underline{H}_3$ protons).
	Acetyl derivative	$CDCl_3$	2.05-3.15 (m; 6 unsymmetrical aromatic protons); 7.62 (S; 3-O.OCC$\underline{H}_3$ Protons); 7.80 (S; 6 two –C$\underline{H}_3$ protons)
C.2	2-(3' Carbmethoxy 4' Hydroxyl benzoyl) 3-nitro Benzoic acid	$CDCl_3$	2.05-2.95 (m, 6 unsymmetrical aromatic protons); 4.25 (S; lactol H); 4.78 (S; 1-Phenolic O$\underline{H}$ proton), 5.90 (S; 3-COOC$\underline{H}_3$protons).
	Acetyl derivative	$CDCl_3$	2.10-2.90 (m; 6 aromatic ring protons); 7.65 (S; 3 lactol –OCO C$\underline{H}_3$ Protons); 7.80 (S; Phenolic 3-OOCC$\underline{H}_3$ protons); 5.90 (S; 3-COOC$\underline{H}_3$ Protons)
C.3	2-(5' Chloro 2' chloro methyl benzoyl)-3-nitro Benzoic acid	DMSO	2.05-3.30 (m; 6 unsymmetrical aromatic protons); 4.30(br; S; lactol $\underline{H}$); 6.55 (S; 2-C$\underline{H}_2$Cl protons)
	Acetyl derivative	DMSO	2.10-3.30 (m; 6 unsymmetrical aromatic protons); 7.62 (S; 3-OOCC$\underline{H}_3$ Protons); 6.52 (S; 2-C$\underline{H}_2$-Cl protons)
C.4	2-(3' acenaphthoyl) -3-nitro benzoic Acid	DMSO	1.90-2.85 (m; 8 unsymmetrical aromatic protons); 7.40 (m; 4-C$\underline{H}_2$-C$\underline{H}_2$ protons); 4.20 (S; lactol H).

NMR SPECTRA OF γ-KETO ACIDS AND THEIR ACETYL DERIVATIVES

	Acids and their acetyl derivatives	Solvent	Chemical shift (τ)
	Acetyl derivative	$CDCl_3$	1.95-2.95 (m; 8 aromatic protons); 7.50 (m; 4-$C\underline{H}_2$-$C\underline{H}_2$ protons); 7.65 (S, 3 –O-OC-$C\underline{H}_3$ protons);
D.1	β-(2,4 dimethyl Benzoyl) propionic Acid	$CDCl_3$	1.90-3.05 (m; 3 unsymmetrical ring protons); 4.30 (br; S; lactol proton); 7.90 (S; 6 two –$C\underline{H}_3$ protons); 9.65 (triplet; 2-$C\underline{H}_2$ ring protons); 8.62 (triplet; 2-CO-$C\underline{H}_2$ ring protons).
	Acetyl derivative	$CDCl_3$	2.15-3.05 (m; 3 unsymmetrical aromatic protons); 7.65 (S; Lactol 3-O.O$C\underline{H}_3$ protons); 9.62 (triplet, 2-$C\underline{H}_2$ ring protons); 8.60 (triplete 2-$COCH_2$ ring protons.
D.2	β-(3 carbmethoxy 4 hydroxy Benzoyl) propionic Acid	$CDCl_3$	1.95-2.85 (m; 3 aromatic ring protons); 4.35(br; S; Lactol –O$\underline{H}$ proton); 9.7 (triplet, 2 -$C\underline{H}_2$ ring products); 8.45 (triplet; 2 –$COC\underline{H}_2$ protons); 4.78 (S; 1 Phenolic –O$\underline{H}$ protons); 5.90 (S; 3 –$COOC\underline{H}_3$ protons).
	Acetyl derivative	$CDCl_3$	2.05-2.90 (m; 3 aromatic ring protons); 7.74(S; 3-$OOCC\underline{H}_3$ protons); 9.80 (triplet, 2 –$C\underline{H}_2$ ring protons); 8.48 (triplet, 2 –$COC\underline{H}_2$ ring protons); 4.80 (S, 1 Phenolic –O$\underline{H}$ protons); 5.90 (S; -$COOC\underline{H}_3$ protons).
D.3	β-(5-chloro 2 Chloro Methyl benzoyl) propionic acid	DMSO	2.10-3.30 (m; 3 aromatic ring protons); 4.35 (br; S; 1 Lactol proton); 9.8 (triplet, 2 -$C\underline{H}_2$ ring protons); 8.7 (triplet, 2 -$C\underline{H}_2$-CO- ring protons) 6.52 (S; two –$C\underline{H}_2$-Cl protons).

	Acids and their acetyl derivatives	Solvent	Chemical shift (τ)
	Acetyl derivative	DMSO	2.05-3.25 (m; 3 aromatic ring protons); 7.65 (S; 3 $-OOCC\underline{H}_3$ protons); 9.75 (triplet, 2 $-C\underline{H}_2$ ring protons); 8.45 (triplet, 2 $-CO-C\underline{H}_2$ ring protons); 6.55 (S; two $-C\underline{H}_2-Cl$ protons).
D.4	β-(3 acenaphthoyl) Propionic acid	DMSO	1.95-2.95 (m; 8 unsymmetrical aromatic protons); 4.20 (br; S; 1 lactol proton); 9.75 (triplet, 2 $-C\underline{H}_2$ ring protons); 8.55 (triplet, 2 $-CO-C\underline{H}_2$ ring protons); 7.40 (m ; 4 $-C\underline{H}_2-C\underline{H}_2-$ ring protons)
	Acetyl derivative	$CDCl_3$	1.95-2.95 (m; 8 unsymmetrical ring protons); 7.70 (S; 3 $-OOCC\underline{H}_3$ protons); 9.8 (triplet, 2 $-C\underline{H}_2$ ring protons); 8.60 (triplet, 2 $-COC\underline{H}_2$ ring Protons); 7.40 (m, 4 $-C\underline{H}_2-C\underline{H}_2-$ ring Protons).

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EXPERIMENTAL

During the investigations leading to this presentation four series of γ-keto acids were synthesized. As already described in Chapter II the labels A, B, C and D have indicated the four series. The acids of A,B & C series were condensed with various aromatic hydroxy compounds to get novel analogues of phthaleins. The members of D series acids i.e. β-aroyl propionic acids were condensed with different phenolic compounds to obtain novel analogues of succineins. The experimental part of the investigations has, therefore, been reported in four chapters as per the following scheme:

Chapter III Experimental A (for dyes obtained from A series of γ-keto acids)

Chapter IV Experimental B (for dyes obtained from B series of γ-keto acids)

Chapter V Experimental C (for dyes obtained from C series of γ-keto acids)

Chapter VI Experimental D (for dyes obtained from D series of β-aroyl propionic acids)

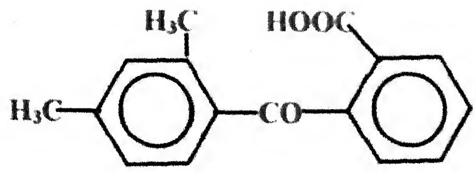
CHAPTER

THREE

EXPERIMENTAL-A

Chapter III

DYES DERIVED FROM 2-(2'4' DIMETHYL BENZOYL) BENZOIC ACID:



A.1 Preparation of 2-(2'4'dimethyl benzoyl) benzoic acid

The acid was prepared by carrying out Friedel-Craft reaction between m Xylene (dry AR 100ml.) and phthalic anhydride (19.5g, 0.1mole) with anhydrous aluminium chloride (27g, 0.2mole) used as catalyst. The reaction was carried out in one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 35 degree centigrade by adding anhydrous aluminium chloride in instalments. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until the evaporation of hydrogen chloride ceased.

The heavy dark coloured complex was decomposed by adding 30 ml of concentrated hydrochloric acid (in 250 ml ice cold water). The excess of m-Xylene was removed by distillation. The residue was extracted three four times with boiling 10% solution of Na_2CO_3 and filtered. The acid was precipitated from the filtrate by the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and crystallized from acetone. The white crystalline acid has m.p. 157-159^0 C, yield 15g. It is soluble in ether, acetone and methanol.

Anal. For : $C_{16}H_{14}0_3$ (molecular weight 254)

Calc. : C, 75.59; H, 5.51;

Found : C, 75.51; H, 5.48;

A.1.1 Prepration of acetyl derivative:

The acid (1.2 g) and fused sodium acetate (3.5g) were refluxed with 20ml of freshly distilled acetic anhydride at 120-130^{0}C for four hours. The hot contents

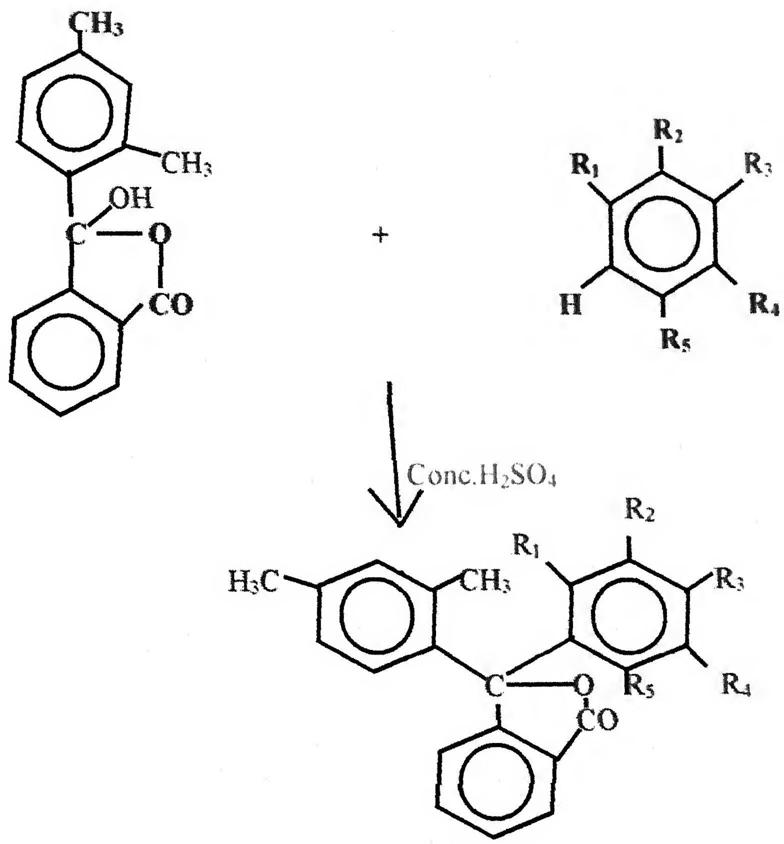
were poured into a beaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of brown coloured solid mass. The coloured acid derivative was decolourized by treatment with animal charcoal. It was crystallized from acetone in the form of amorphous solid; m.p 88-90^{0}C .It is soluble in acetone, chloroform and acetic acid, yield 0.75g.

Anal. For : $C_{18}H_{16}O_4$ or $C_{16}H_{13}O_3$ ($OC.CH_3$) (molecular wt. 296)

Calc. : C, 72.97; H, 5.41; acetyl, 14.53;

Found : C,72.90; H, 5.38 ; acetyl, 14.49

The dyes prepared from the acid may be represented by the following structures.



A.1.2 (2, 4 dimethyl phenyl) phenol phthal-as-ein
$R_1 = R_2 = R_4 = R_5 = H, R_3 = OH$

A.1.3 (2, 4 dimethyl phenyl) resorcinol phthal-as-ein
$R_2 = R_4 = R_5 = H, \ R_1 = R_3 = OH$

A.1.4 (2, 4 dimethyl phenyl) catechol phthal-as-ein
$R_3 = R_4 = R_5 = H, \ R_1 = R_2 = OH$

A.1.5 (2, 4 dimethyl phenyl) hydroquinone phthal-as-ein
$R_2 = R_3 = R_5 = H, \ R_1 = R_4 = OH$

A.1.6 (2, 4 dimethyl phenyl) pyrogallol phthal-as-ein
$R_4 = R_5 = H, \ R_1 = R_2 = R_3 = OH$

A.1.7 (2, 4 dimethyl phenyl) phloroglucinol phthal-as-ein
$R_2 = R_4 = H, \ R_1 = R_3 = R_5 = OH$

A.1.8 (2, 4 dimethyl phenyl) diacetyl resorcinol phthal-as-ein
$R_2 = R_4 = R_5 = H, \ R_1 = R_3 = OCOCH_3$

A.1.9 (2, 4 dimethyl phenyl) dibromo resorcinol phthal-as-ein
$R_5 = H, R_1 = R_3 = OH; \ R_2 = R_4 = Br$

A.1.2 Preparation of (2,4 dimethyl phenyl)-phenol-phthal-as-ein:

The acid (1.5g) and phenol (1.0g) were condensed in an oil bath in presence of 4-5 drops of concentrated sulphuric acid at 160-170^0 C for about four and a half hours till the molten mass of the tube became brittle on cooling. The condensed mass was taken out from the coloured tube and subjected to steam distillation to remove excess of phenol. The buff coloured solid mass left in the flask was powdered and extracted with 2% NaOH solution. It was filtered and the dye was precipitated from filtrate by the gradual addition of hydrochloric acid with constant stirring. It was purified by repeated crystallization from rectified spirit and dried in a vacuum desiccator, yield, 1.1g.

The purity of the dye was tested by paper chromatography by descending technique.

Paper	Whatman No 1
Mobile phase	Butanol saturated with ammonia

Developing agent 1% aqueous caustic soda

Reference dye Phenolphthalein

A-25cm x 10-cm strip was taken and a very dilute solution of the dye was spotted on the paper (on a base line 4.0 cm from the end) with micro syringe. Similarly, a dilute aqueous solution of the reference dye was also spotted on the base line about 3.0 cm from the first spot. The mobile phase was allowed to run for thirteen hours. The paper was then taken out, dried and sprayed. Chromatogram of each dye gave only one corresponding spot. This confirmed the homogeneity and purity of the dye.

Found	: R_f (phenolphthalein): 0.93
	: R_f [(2,4 dimethyl phenyl) phenol phthal-as-ein]:0.94
Reported	: R_f (phenolphthalein):0.92

The brown coloured micro-crystalline dye, m.p 178-180^{0}C gives light yellow colour in ethanol which turns into pink on adding a drop of an alkali. It is soluble in benzene, acetone and ethanol.

Anal. For : $C_{22}H_{18}O_3$, (molecular weight 330)

Calc. : C, 80.0, H , 5.45;

Found :C, 79.92, H, 542.

A.1.3 PREPARATION OF (2, 4 DIMETHYL) - PHENYL RESORCINOL-PATHAL-AS-EIN:

It was prepared by condensing an intimate mixture of the acid (5.0 g) and resorcinol (3.0g) in the oil bath in presence 4-5 drops of concentrated sulphuric acid at 145-150^{0}C for about four and half hours till the molten mass became hard and brittle on cooling. The condensed mass was crushed and washed with an excess of water to remove excess of resorcinol. It was extracted with 2% aqueous solution of caustic soda and filtered. The dye was precipitated from reddish brown with green fluorescent by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 100^{0}C and then in a vacuum desiccators, yield 5.4g.

The orange yellow microcrystalline dye having m.p. 156-158^{0}C is, soluble

in benzene, ethanol, methanol and acetic acid. Its ethanolic solution is yellow which alters to brownish yellow with green fluorescence on adding a drop of an alkali. In strong basic medium, reddish brown colour is obtained.

Anal. For	: $C_{22}H_{18}O_4$ (molecular weight 346)
Calc.	: C, 76.30; H, 5.20;
Found	: C, 76.19; H, 5.18;

A.1.4 Preparation of (2,4 dimethyl phenyl)-catechol-phthal-as-ein:

The dye was prepared by heating a homogeneous mixture of the acid (1.2g) and catechol (1.5g) in an oil bath 120-130^{0}C in presence of 4-5 drops of concentrated sulphuric acid for about four hours. The isolation and purification of the dye were done as in the case of (2, 4 dimethyl phenyl) resorcinol phthal-as-ein, Yield 1.8g. The dye is black in colour, m.p. above 360^{0}C. Its ethanolic solution is slightly brown in colour. It gives deep black colour on addition of alkali. It is soluble in acetone, ethanol an acetic acid.

Anal. For	: $C_{22}H_{18}O_4$ (molecular weight 346)
Calc.	: C, 76.30; H, 5.20;
Found	: C, 76.22; H, 5.17;

A.1.5 Preparation of (2,4 dimethyl phenyl) hydroquinone phthal-as-ein:

It was prepared by condensing a homogeneous mixture of the acid (1.5g) and hydroquinone (1.5g). The intimate mixture was heated on oil bath at 140-150^{0}C in presence of 4-5 drops of concentrated sulphuric acid for about four hours till the molten mass became hard and brittle on cooling. The isolation and purification of the dye were done as in the case of (2, 4 dimethyl phenyl) resorcinol phthal-as-ein, yield 1.6g.

The black coloured dye having m.p. above 360^{0}C, is soluble in chloroform, ethanol and methanol. Its alcoholic solution gives a golden yellow colour that turns into dark brown on addition of an alkali.

Anal. For	: $C_{22}H_{18}O_4$ (molecular weight 346)

Calc. : C, 76.30; H, 5.20;

Found : C, 76.21; H, 5.15;

A.1.6 Preparation of (2,4 dimethyl phenyl) pyrogallol phthal-as-ein:

The mixture of the acid (1.0g) and pyrogallol (1.2g) was heated on the oil bath in presence of 4-5 drops of concentrated sulphuric acid at 130-150^{0}C for about four hours. The dye was isolated and purified in a manner similar to the other dyes, yield 1.2g.

The black shining crystals having a m.p. above 360^{0}C, is soluble in ethanol, methanol and acetic. It dissolves in ethanol yielding wine colour which turns violet on addition of a drop of an alkali.

Anal. For : $C_{22}H_{18}O_5$ (molecular weight 363)

Calc. : C, 72.93; H, 4.97;

Found : C, 72.84; H, 4.93;

A.1.7 Preparation of (2,4 dimethyl phenyl) phloroglucinol phtha-as-ein:

It was prepared by condensing a homogenous mixture of the acid (1.2g) and phloroglucinol (1.5g). The intimate mixture was heated on oil bath at 190-210^{0}C for about four hours. The dye was isolated and purified in a manner similar to the other dyes, yield 1.0g.

The dark brown dye m.p. > 360^{0}C, gives lemon yellow colour with ethanol, which turns into orange on adding a drop of an alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal. For : $C_{22}H_{18}O_5$ (molecular weight 362)

Calc. : C, 72.93; H, 4.97;

Found : C, 72.81; H, 4.92;

A.1.8 Preparation of (2,4 dimethyl phenyl) diacetyl resorcinol phthal-as-ein:

[Acetylation of (2,4 dimethyl phenyl) resorcinol phthal-as-ein]

The dye (2,4 dimethyl phenyl) resorcinol phthal-as-ein (1.0g) and fused sodium acetate (3.0g) with 15.0 ml of freshly distilled acetic anhydride were taken in a 50 ml round bottom flask fitted with an air condenser. The contents were refluxed at 125-135^{0}C for about four hours. The hot contents poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon the light yellow solid settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallized from aqueous ethanol and a little acetic acid. It was dried in an oven at 40^{0}C and then over phosphorus pentoxide under reduced pressure, yield 0.65g.

The crystalline derivative is light yellow coloured and has a m.p. of 110-112^{0}C. It is soluble in benzene, ether, chloroform and acetic acid.

Anal. For	: $C_{26}H_{22}O_6$ or $C_{22}H_{16}O_4(OC.CH_3)_2$ (molecular weight 430)
Calc.	: C, 72.56; H, 5.12; Acetyl, 20.00;
Found	: C, 72.47; H, 5.08; Acetyl, 19.94;

4.1.9 Bromination of (2,4 dimethyl phenyl) resorcinol phthal-as-ein:

[(2,4 dimethyl phenyl) dibromo resorcinol phthal-as-ein]

The dye (2,4-dimethyl phenyl)-resorcinol-phthal-as-ein (1.0g) was dissolved in minimum quantity of glacial acetic acid and 15ml of a 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130^{0}C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dirty orange powder settled down. It was filtered and washed well with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye by gradual addition of dilute hydrochloric acid. The crude brominated dye was finally purified by crystallization from aqueous ethanol and dried at 80^{0}C in and oven and then in a vacuum desiccators, yield, 1.3g.

The dirty orange crystalline compound having m.p. 90-91^{0}C is soluble in benzene, ether, chloroform, acetone and acetic acid.

Anal. For	: $C_{22}H_{16}Br_2O_4$ (molecular weight 504)
Calc.	: Br, 31.75;

Found : Br, 31.68;

A.1.10 Caustic Potash treatment of (2,4 dimethyl phenyl) resorcinol phthal-as-ein:

Potassium hydroxide pallets (10.0g) were taken in a crucible and heated with a few drops of water to make a paste. The dye (1.0) was then added to it. The contents were heated for about four hours till the darkened colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. The dark residue (I) settled down on just neutralizing the alkali. It was filtered and washed well with water. The filtrate, when acidified further by adding excess of dilute hydrochloric acid gave white precipitate (II), which was filtered and washed with water. It was crystallized from aqueous ethanol and dried in a vacuum desiccators. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Residue-I

It was identified and confirmed to be the unreacted dye from its colour reaction and determination of the mixed melting point with the authentic sample.

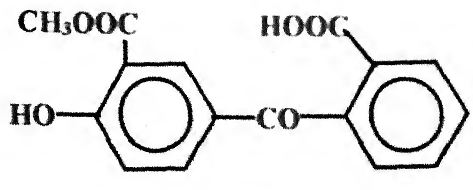
Residue-II

It was acidic in nature and gave positive tests for the presence of carboxylic groups. It was identified as 2-(2' 4' dimethyl benzoyl) benzoic acid and confirmed by mixed melting point determination (m.p.157-159^{0}C) and by superimposition of the IR spectra of the authentic sample.

Residue-III

The purified sample melted at 109-110^{0}C. It gave positive tests with ferric chloride, Fehling's solution and ammoniacal silver nitrate. It gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol. Acetylation, bromination and caustic potash treatment of the dye are shown in chart A in chapter II.

DYES DERIVED FROM 2-(3' CARBMETHOXY 4' HYDROXY BENZOYL) BENZOIC ACID:



A.2 Preparation of 2-(3' carbmethoxy 4' hydroxy benzoyl) benzoic acid:

The acid was prepared by carrying out Friedel-Crafts reaction between methyl salicylate (dry AR 100ml) and phthalic anhydride (19.5g, 0.1mole) with anhydrous aluminium chloride (27g, 0.2mole) used as a catalyst. The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 35 degree centigrade by adding anhydrous aluminium chloride in instalments. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until the evaporation of hydrogen chloride ceased.

The heavy dark coloured complex was decomposed adding 30 ml of concentrated hydrochloric acid (in 250 ml ice cold water). The residue was extracted three four times with boiling 10% solution of $Na_2\ CO_3$ and filtered. The acid was precipitated from the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and crystallized from acetone. The white crystalline acid has m.p. 170-172^{0}C, yield 15 g. It is soluble in ether, acetone and methanol.

Anal. for	$C_{16}H_{12}O_6$ (molecular weight 300)
Calc.	C, 64.0; H, 4.0;
Found	C, 63.84; H, 3.96;

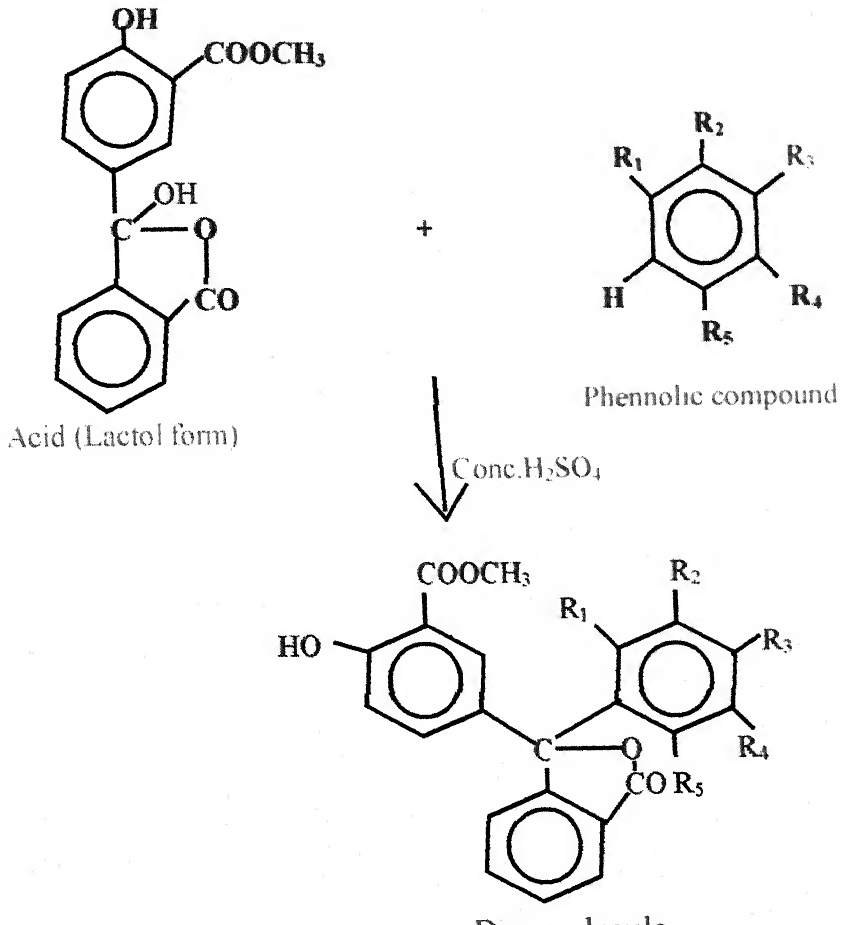
A.2.1 Preparation of acetyl derivative:

The acid (1.2g) and fused sodium acetate (3.5g) were refluxed with 20 ml of freshly distilled acetic anhydride at 120-130^{0}C for four hours. The hot contents were poured into a beaker containing ice cold water with constant stirring. The

acetyl derivative settled down in the form of brown coloured solid mass. The coloured acid derivative was decolorized by treatment with animal charcoal. It was crystallized from acetone in the form of amorphous solid, m.p. 112°C (decomposed). It is soluble in acetone chloroform and acetic acid, yield 0.75 g.

Anal. for	$C_{20}H_{16}O_6\ (OCCH_3)_2$ (molecular weight 384)
Calc.	C, 62.50; H, 4.17; acetyl, 22.40;
Found	C, 62.39; H, 4.14; acetyl 22.32;

The dyes prepared from the acid may be represented by the following structures.



Dye molecule

A.2.2 (3 carbmethoxy 4-hydroxy phenyl) phenol phthal-as-ein.
$R_1 = R_2 = R_4 = R_6 = H, R_3 = OH$

A.2.3 (3 carbmethoxy 4 hydroxyl phenyl) resorcinol phthal-as-ein.
$R_2 = R_4 = R_5 =$ H, $R_1 = R_3 =$ OH

A.2.4 (3 carbmethoxy 4 hydroxy phenyl) catechol phthal-as-ein
$R_3 = R_4 = R_5 =$ H, $R_1 = R_2 =$ OH

A.2.5 (3 carbmethoxy 4 hydroxy phenyl) hydroquinone phthal-as-ein.
$R_2 = R_3 = R_5 =$ H, $R_1 = R_4 =$ OH

A.2.6 (3 carbmethoxy 4 hydroxy phenyl) pyrogallol phthal-as-ein
$R_4 = R_5 =$ H, $R_1 = R_2 = R_3 =$ OH

A.2.7 (3 carbmethoxy 4 hydroxy phenyl) phloroglucinol phthal-as-ein
$R_2 = R_4 =$ H, $R_1 = R_3 = R_5 =$ OH

A.2.8 (4 acetoxy 3 carbmethoxy phenyl) diacetyl resorcinol phthal-as-ein
$R_2 = R_4 = R_5 =$ H, $R_1 = R_3 = OCOCH_3$

A.2.9 (3 bromo 5 carbmethoxy 4 hydroxy phenyl) dibromo resorcinol phthal-as-ein
$R_5 =$ H, $R_1 = R_3 =$OH, $R_2 = R_4 =$ Br

A.2.2 Preparation of (3- carbmethoxy 4- hydroxy phenyl)-phenol-phthal-as-ein:

The acid (1.5g) and phenol (1.0g) were condensed in an oil bath in presence of 4-5 drops of concentrated sulphuric acid at 160-170^{0}C for about four and a half hours till the molten mass of the tube became brittle on cooling. The condensed mass was taken out from the coloured tube and subjected to steam distillation to remove excess of phenol. The buff coloured solid mass left in the flask was powdered and extracted with 2% NaOH solution. It was filtered and the dye was precipitated from filtrate by the gradual addition of hydrochloric acid with constant stirring. It was purified by repeated crystallization from rectified spirit and dried in a vacuum desiccator, yield, 1.1g.

The purity of the dye was tested by paper chromatography.

Paper	Whatman No 1
Mobile phase	Butanol saturated with ammonia

Developing agent 1% aqueous caustic soda

Reference dye Phenolphthlein

A 25-cm x 10-cm strip was taken and a very dilute solution of the dye was spotted on the paper (on a base line 4.0 cm from the end) with a micro syringe. Similarly, a dilute aqueous solution of the reference dye was also spotted on the base line about 3.0 cm from the first spot. The mobile phase was allowed to run for thirteen hours. The paper was then taken out, dried and sprayed. Chromatogram of each dye gave only one corresponding spot. This confirmed the homogeneity and purity of the dye.

Found : R_f (phenolphthalein) : 0.93

: R_f [3-carbmrthoxy 4 hydroxy phenyl) phenol phthal-as-ein]: 0.94

Reported : R_f (phenolphthalein): 0.92

The orange coloured micro-crystalline dye, m.p. 126-127^{0}C gives light brownish red colour in ethanol which turns into pink on adding a drop of an alkali. It is soluble in benzene, acetone and ethanol.

Anal. for : $C_{22}H_{16}O_6$ (molecular weight 376)

Calc. : C, 70.22; H, 4.25;

Found : C, 70.10; H, 4.21;

A.2.3 Preparation of (3- carbmethoxy 4- hydroxy phenyl)-resorcinol-phthal-as-ein:

It was prepared by condensing an intimate mixture of the acid (3.0g) and resorcinol (2.0g) in the oil bath in presence of 4-5 drops of concentrated sulphuric acid at 145-150^{0}C for about four and half hours till the molten mass became hard and brittle on cooling. The condensed mass was crushed and washed with an excess of water to remove excess of resorcinol. It was extracted with 2% aqueous solution of caustic soda and filtered. The dye was precipitated from reddish brown with green fluorescent filtrate by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 100^{0}C and then in a vacuum desiccator, yield 2.5 g.

The red microcrystalline dye having m.p. 183-185°C, is soluble in benzene, ethanol, methanol and chloroform. Its ethanolic solution is golden which alters to reddish yellow with green fluorescence on adding a drop of an alkali. In strong basic medium, reddish brown with green fluorescence colour is obtained.

Anal. for	$C_{22}H_{16}O_7$ (molecular weight 392)
Calc.	C, 67.35; H, 4.08;
Found	C, 67.24; H, 4.05;

A.2.4 Preparation of (3 carbmethoxy 4 hydroxyl phenyl)-catechol-phthal-as-ein:

The dye was prepared by heating homogeneous mixture of the acid (1.2g) and catechol (1.5g) in an oil bath at 120-130°C in presence of 4-5 drops of concentrated sulphuric acid for about four hours. The isolation and purification of the dye were done as in the case of (3 - carbmethoxy 4 - hydroxyl phenyl) resorcinol phthal-as-ein. Yield 1.8g.

The dye is black in colour decomposes above 300°C its ethanolic solution is slightly brown in colour. It gives brown colour on addition of alkali. It is soluble in methanol ethanol and acetic acid.

Anal. for	$C_{22}H_{16}O_7$ (molecular weight 392)
Calc.	C, 67.35; H, 4.08;
Found	C, 67.20; H, 4.02;

A.2.5 Preparation of (3- carbmethoxy 4- hydroxy phenyl) hydroquinone phthal-as-ein:

It was prepared by condensing a homogeneous mixture of the acid (1.5g) and hydroquinone (1.5g). The intimate mixture was heated on oil bath at 140-150°C in presence of 4-5 drops of concentrated sulphuric acid for about four hours till the molten mass became hard and brittle on cooling. The isolation and purification of the dye were done as in the case of (3 - carbmethoxy 4 - hydroxyl phenyl) resorcinol phthal-as-ein. Yield 1.6 g.

The black coloured dye having m.p. above 300°C, is soluble in chloroform,

ethanol and methanol. Its alcoholic solution gives a crimson colour that turns into dark brown on addition of an alkali.

Anal. for	$C_{22}H_{16}O_7$ (molecular weight 392)
Calc.	C, 67.35; H, 4.08;
Found	C, 67.20; H, 4.04;

4.2.6 Preparation of (3- carbmethoxy 4- hydroxy phenyl) pyrogallol phthal-as-ein:

The mixture of the acid (1.0g) and pyrogallol (1.2g) was heated in an oil bath in presence of 4-5 drops of concentrated sulphuric acid at 130-150^{0}C for about four hours. The dye was isolated and purified in a manner similar to the other dyes, yield 1.2g.

The black shining crystals having a m.p. above 360^{0}C, is soluble in ethanol, methanol and acetic acid. It dissolves in ethanol yielding wine red colour which turns violet on addition of a drop of an alkali.

Anal. for	$C_{22}H_{16}O_8$ (molecular weight 408)
Calc.	C, 64.71; H, 3.92;
Found	C, 64.60; H, 3.88;

4.2.7 Preparation of (3-carbmethoxy 4-hydroxy phenyl) phloroglucinol phthal-as-ein:

It was prepared by condensing a homogeneous mixture of the acid (1.2g) and phloroglucinol (1.5g). The intimate mixture was heated on oil bath at 190-210^{0}C for about four hours. The dye was isolated and purified in a manner similar to the other dyes, yield 1.0g.

The dark orange dye m.p. > 360^{0}C, gives golden yellow colour with ethanol, which turns into reddish orange on adding a drop of an alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal. for	$C_{22}H_{16}O_8$ (molecular weight 408)
Calc.	C, 64.71; H, 3.92;

Found C, 64.62; H, 3.89;

4.2.8 Preparation of (4-acetoxy 3- carbmethoxy phenyl) diacetyl resorcinol phthal-as-ein:

[Acetylation of 3-carbmethoxy 4-hydroxyl phenyl) resorcinol phthal-as-ein]

The dye (3-cabmethoxy 4-hydroxyl phenyl) resorcinol phthal-as-ein (1.0g) and fused sodium acetate with 15.0 ml of freshly distilled acetic anhydride were taken in a 5 ml round bottom flask fitted with an air condenser. The contents were refluxed at 125-135^{0}C for about four hours. The hot contents were poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon the light yellow solid settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallized from aqueous ethanol and a little acetic acid. It was dried in an oven at 40^{0}C and then over phosphorus pentoxide under reduced pressure, yield 0.65g.

The crystalline acetyl derivative is light yellow coloured and has a m.p. 200-202^{0}C. It is soluble in benzene, ether, chloroform and acetic acid.

Anal. for	$C_{28}H_{22}O_{10}$ or $C_{22}H_{13}O_7$ $(OCCH_3)_3$ (mol. wt. 518)
Calc.	C, 64.86; H, 4.25; Acetyl 24.90;
Found	C, 64.70; H, 4.20; Acetyl 24.82;

4.2.9 bromination of (3- carbmethoxy 4- hydroxy phenyl) resorcinol phthal-as-ein:

[(3-bromo 5-carbmethoxy 4-hydroxyl phenyl) dibromo resorcinol phthal-as-ein]

The dye (3-carbmethoxy 4-hydroxyl phenyl)-resorcinol-phthal-as-ein (1.0g) was dissolved in minimum quantity of glacial acetic acid and 15 ml of a 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130^{0}C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dirty orange powder settled down. It was filtered and washed well with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude brominated dye was finally

purified by crystallization from aqueous ethanol and dried at 80°C in an oven and then in a vacuum desiccator, yield 1.2g.

The pale orange crystalline dye having m.p. 256-257°C is soluble in benzene, ether, chloroform, acetone and acetic acid.

Anal. for	$C_{22}H_{13}Br_3O_7$ (molecular weight 629)
Calc.	Br, 38.16;
Found	Br, 38.04;

4.2.10 Caustic potash treatment of (3- carbmethoxy 4- hydroxy phenyl) resorcinol phthal-as-ein:

Potassium hydroxide pellets (10.0g) were taken in a crucible and heated with a few drops of water to make a paste. The dye (1.0) was then added to it. The contents were heated for about four hours till the darkened colour of the dye faded completely. After cooling, the contents were diluted with 50 ml of water and filtered. The dark residue (I) settled down on just neutralizing the alkali. It was filtered and washed well with water. The filtrate, when acidified further by adding excess of dilute hydrochloric acid gave white precipitate (II), which was filtered and washed with water. It was crystallized from aqueous ethanol and dried in a vacuum desiccator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Residue-I

It was identified and confirmed to be the unreacted dye from its colour reactions and determination of the mixed melting point with the authentic sample.

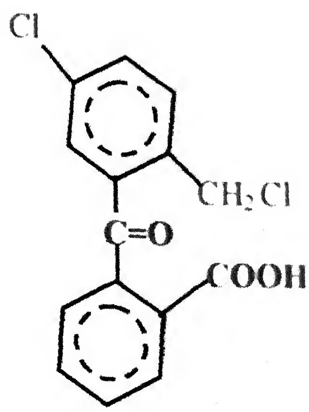
Residue-II

It was acidic in nature and gave positive tests for the presence of carboxylic and phenolic groups. It was identified as 2-(3' carbmethoxy 4' hydroxy benzoyl) benzoic acid and confirmed by mixed melting point determination (m.p. 170-172°C) and by superimposition of the IR spectra of the authentic sample.

Residue – III

The purified sample melted at 109-110°C. It gave positive tests with ferric chloride, Fehling's solution and ammoniacal silver nitrate. It gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol. Acetylation, bromination and caustic potash treatment of the dye are shown in chart C in chapter II.

DYES DERIVED FROM 2-(5' CHLORO 2' CHLOROMETHYL BENZOYL) BENZOIC ACID:



(5'- chloro 2'- chloromethyl benzoyl) benzoic acid

A.3 PREPATION OF 2- (5' CHLORO 2' CHLOROMETHYL BENZOYL) BENZOIC ACID:

The acid[4] was prepared by carrying out the Friedel Craft's reaction between 100ml of AR dry 4- chloro benzyl chloride and 15.0g (about 0.1 mole) of phthalic anhydride in presence of 27.0g of anhydrous aluminum chloride (about 0.2 mole) as catalyst in a similar manner as 2-(2' 4' dimethyl benzoyl) benzoic acid. The acid was crystallized from hot water in the form of a white crystalline solid with m.p. 188-190^0 C. The acid was found to be soluble in methanol and sparingly soluble in acetone. The yield was found to be 14.0g.

Anal for	: $C_{15}H_{10}Cl_2O_3$ (mol. Wt. 309)
Calc.	: C, 58.25; H, 3.24; Cl, 22.98;
Found	: C, 58.12; H, 3.20; Cl, 22.90;

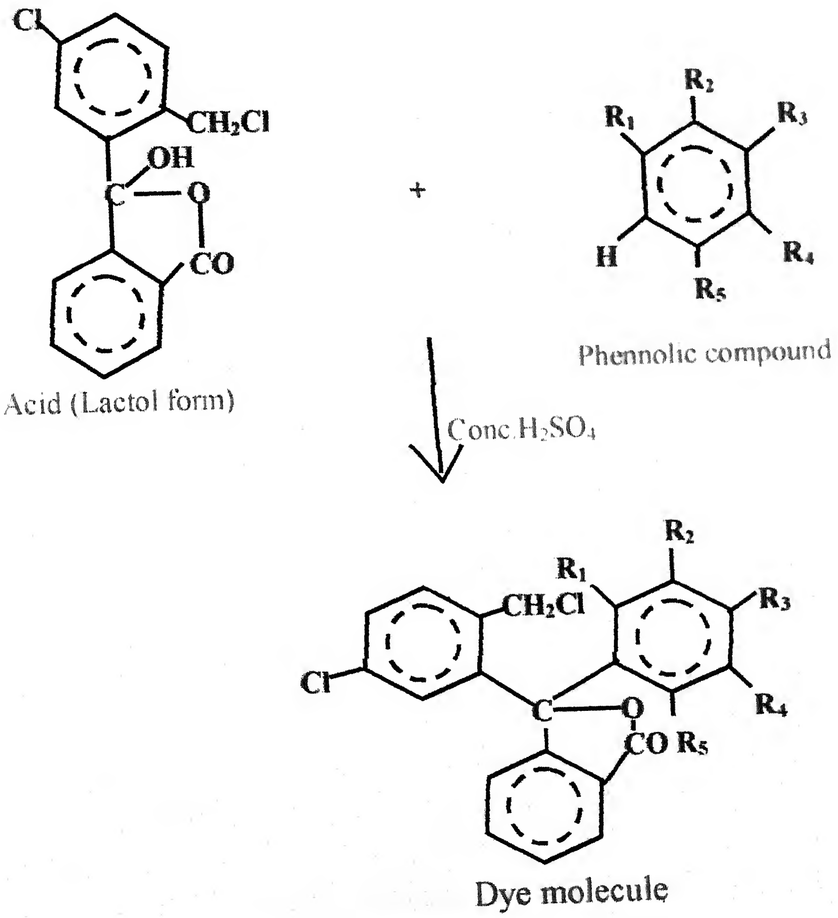
A.3.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

It was prepared by taking 1.0g of the acid and 3.0g of fused sodium acetate and refluxing them with 15ml of freshly distilled acetic anhydride at 120-130^0 C in a similar manner as in the case of acetyl derivative of 2-(2' 4' dimethyl

benzoyl) benzoic acid. The acetyl derivative settled down in the form of a coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with charcoal and filtered while hot. It was recrystallised from acetone in the form of a light brown solid, m.p. 126-128^{0}C. It is soluble in acetone, chloroform, ethanol and acetic acid. Yield 0.68g.

Anal for	: $C_{17}H_{12}Cl_2O_4$ (mol. wt. 351)
Calc.	: C, 58.12; H, 3.42; Cl, 20.23; acetyl. 12.25;
Found	: C, 58.00; H, 3.38; Cl, 20.10; acetyl 12.15;

The dyes prepared from the acid may be represented by the following structures:



DYES:

A.3.2 (5- chloro-2- chloromethyl phenyl) phenol phthal-as-ein:
$R_1 = R_2 = R_4 = R_5 = H, R_3 = OH$

A.3.3 (5- chloro-2- chloromethyl phenyl) resorcinol phthal-as-ein:
$R_2 = R_4 = R_5 = H, \; R_1 =, \; R_3 = OH$

A.3.4 (5- chloro-2- chloromethyl phenyl) catechol phthal-as-ein:
$R_3 = R_4 = R_5 = H, \; R_2 =, \; R_3 = OH$

A.3.5 (5- chloro-2- chloromethyl phenyl) hydroquinone phthal-as-ein:
$R_2 = R_3 = R_5 = H, \; R_1 =, \; R_4 = OH$

A.3.6 (5- chloro-2- chloromethyl phenyl) pyrogallol phthal-as-ein:
$R_4 = R_5 = H, R_1 = \; R_2 =, \; R_3 = OH$

A.3.7 (5- chloro-2- chloromethyl phenyl) phloroglucinol phthal-as-ein:
$R_2 = R_4 = H, R_1 = \; R_3 =, \; R_5 = OH$

A.3.8 (5- chloro-2- chloromethyl phenyl) diacetyl phthal-as-ein:
$R_2 = R_4 = R_5 = H, \; R_1 =, \; R_3 = OCOCH_3$

A.3.9 (5- chloro-2- chloromethyl phenyl) dibromo phthal-as-ein:
$R_5 = H, R_1 = R_3 = OH, R_2 =, \; R_4 = Br$

A.3.2 PREPARATION OF (5- CHLORO 2- CHLOROMETHYL PHENYL) PHENOL PHTHAL-AS-EIN:

A homogenized intimate mixture of 1.5g of the acid and 1.0g of phenol was condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 165-175^0 C for about four hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The buff coloured solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystllisation from rectified spirit and dried in vacuum desiccator, yield 1.5g m.p. 118-119^0 C.

The dark brown coloured dye is soluble in ethanol and rectified spirit. The ethanolic solution of the dye is almost reddish cream in colour which turns into pink on adding a drop of an alkali. In strong basic medium, it gives pink colour.

Anal for	: $C_{21}H_{14}Cl_2O_3$ (mol. Wt. 385)
Calc.	: C, 65.45; H, 3.64; Cl, 18.44;
Found	: C, 65.32; H, 3.60; Cl, 18.32;

A.3.3 PREPARATION OF (5- CHLORO- 2- CHLOROMETHYL PHENYL) RESORCINOL PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 3.0g of the acid and 2.0g resorcinol in an oil bath at 135-145^0 C for four hours in presence of a few drops of concentrated sulphuric acid. The condensed brittle solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the reddish brown with green fluorescent extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated recrystallisation from rectified spirit and dried at 100^0 C and then in vacuum desiccator, yield 5.4g.

The dye is red, crystalline in nature having m.p. 268-269^0 C. It yield a golden yellow colour with fluorescence in ethanol which turns to reddish yellow with green fluorescence on adding a drop of an alkali.

Anal for	: $C_{21}H_{14}Cl_2O_4$ (mol. wt. 401)
Calc.	: C, 62.84; H, 3.49; Cl, 17.71;
Found	: C, 62.62; H, 3.40; Cl, 17.60;

A.3.4 PREPARATION OF (5- CHLORO- 2- CHLOROMETHYL PHENYL) CATECHOL PHTHAL-AS-EIN:

It was prepared by the condensation of 1.0g of the acid and requisite amount of catechol on an oil bath in presence of 5-6 drops concentrated sulphuric acid for about three and half hours at 125-135^0 C. The condensed mass was crushed and washed with an excess of water to remove excess of catechol. It was isolated and purified as done for the corresponding phenol dye, yield 0.8g.

The black powdery dye having a m.p. > 360^0 C. It dissolves in ethanol giving a brownish black coloured solution that darkens on adding a drop of an alkali.

Anal for	: $C_{21}H_{14}Cl_2O_4$ (mol. wt. 401)
Calc.	: C, 62.84; H, 3.49; Cl, 17.71;
Found	: C, 62.68; H, 3.44; Cl, 17.60;

A.3.5 PREPARATION OF (5- CHLORO- 2- CHLOROMETHYL PHENYL) HYDROQUINONE PHTHAL-AS-EIN:

1.0g of the acid and 1.0g of hydroquinone was ground into an intimate mixture and was treated in an oil bath at 160-175^0 C for four hours in presence of four five drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for (5-chloro -2-chloromethyl phenyl) resorcinol phthal-as-ein described earlier, yield 0.85g.

The black coloured powdery dye, decomposing above 360^0 C is soluble ethanol, methanol, chloroform and acetic acid. Its ethanolic solution is brown in colour that turns blackish brown on the addition of a drop of an alkali.

Anal for	: $C_{21}H_{14}Cl_2O_4$ (mol. wt. 401)
Calc.	: C, 62.84; H, 3.49; Cl, 17.71;
Found	: C, 62.58; H, 3.43; Cl, 17.58;

A.3.6 PREPARATION OF (5- CHLORO- 2- CHLOROMETHYL PHENYL) PYROGALLOL PHTHAL-AS-EIN:

The intimate and homogeneous mixture of 1.0g of the acid and 1.0g of pyrogallol were mixed to make a homogeneous mass and ~~the~~ condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 135-145^0 C for about four hours till the melt became hard and brittle. The procedure adopted for isolation and purification of the dye was similar to the one adopted for (5-chloro-2-chloromethyl phenyl) resorcinol phthal-as-ein, yield 0.8g.

Anal for	: $C_{21}H_{14}Cl_2O_5$ (mol. wt. 417)
Calc.	: C, 60.43; H, 3.36; Cl, 17.03;

Found : C, 60.30; H, 3.32; Cl, 17.00;

A.3.7 PREPARATION OF (5-CHLORO-2-CHLOROMETHYLPHENYL) PHLOROGLUCINOL PHTHAL-AS-EIN:

The homogenous mixture of 1.0g of acid , 1.0g phluroglucinol were mixed intimately to make a homogenous mixture and along with a few drops of concentrated sulphuric acid as condensing agent was heated on an oil bath at 200-220^0 C for about four hours. The isolation and purification of the dye was performed in the same way as that described for (5-chloro-2-chloromethylphenyl) resorcinol phthal-es-ein, yield 0.80g.

The reddish brown dye m.p. 180^0 C (decomp.) yields a golden yellow coloured solution in ethanol that turns dark red on adding a drop of an alkali.

Anal. For : $C_{12}H_{14}C_{l2}O_5$ (mol. wt. 417)

Calc : C, 60.43; H, 3.36; Cl, 17.03;

Found : C, 60.28 ; H , 3.30 ; Cl, 17.00;

A.3.8 ACETYLATION OF (5-CHLORO-2-CHLOROMETHYLPHENYL) RESORCINOLN PHTHAL-AS-EIN:

[(5-CHLORO-2-CHLOROMETHYLPHENYL) DIACETYL RESORCINOL PHTHAL-AS-EIN]

1.0g of the dye, 3.0g fused sodium acetate and 15 ml of freshly distilled acetic anhydride were taken in a 50 ml round bottom flask fitted with an air condenser. The contents were refluxed at 130-140^0 C for about four hours. The hot contents were poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon a light yellow solid settled down. It was filtered, washed well and dried. The crude products was treated with animal charcoal and finally crystallized from aqueous ethanol in presence of a drop of acetic acid. It was dried in an oven at 70^0 C and then phosphorous pentaoxide under reduced pressure. Yield 0.75g.

The pale yellow coloured diacetyl derivative (m.p. 184-186^{0}C) is soluble in ethanol, methanol, chloroform and acetic acid.

Anal. For : $C_{25}H_{18}Cl_2O_6$ or $C_{21}H_{12}Cl_2O_4\,(OC.CH_3)_2$ (mol. wt .485)

Calc : C, 61.86; H, 3.71 ; Cl, 14.64; acetyl, 17.73;

Found : C, 61.60; H, 3.67; Cl, 14.60; acetyl, 17.67;

A.3.9 BROMINATION OF (5-CHLORO-2-CHLOROMETHYLPHENYL) RESORCINOL PHTHAL-AS-EIN:

[PREPARATION OF (5-CHLORO-2-CHLOROMETHYLPHENYL) DIBROMO RESORCINOL PHTHAL-AS-EIN

The 1.0g of the dye (5-chloro-2-chloromethylphenyl) resorcinol phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10% solution of bromine in glacial acetic acid was slowly and gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130^0 C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dark orange substance settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in a dilute aqueous solution of caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo drivayive of the dye was finally purified with aqueous ethanol and dried at 110^0 C in an oven and then in vacuum desiccator, yield 0.92g.

The dark orange crystalline and dye having m.p. 294-296^0 C is soluble in methanol, Ethanol and acetone.

Anal. for : $C_{21}H_{12}Br_2Cl_2O_4$ (mol. wt 559)

Calc : Br, 28.62;

Found : Br, 28.50;

A.3.10 CAUSTIC POTASH TREATMENT OF (5-CHLORO-2-CHLOROMETHYLPHENYL) RESORCINOL PHTHAL-AS-EIN:

10.0g of potassium hydroxide pellets were placed in a crucible and heated in a sand bath with a few drops of water to turn them into a paste. 1.0g of the dye was then added to the crucible and contents were heated for about three and a half hours till the colour of the dye faded completely. After cooling, the contents were diluted with 50 ml of water and filtered. A dark orange residue (I) settled

down on just neutralizing the alkali. It was filtered and washed with water. The filtrate when acidified further by adding dilute hydrochloric acid gave a white precipitate (II) that was filtered and washed with water. It was recrystallised from aqueous ethanol and dried in a vacuum desiccator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a dark orange residue (III) was obtained.

Identification of residue I :

It was identified and confirmed as the unreacted residual dye from the colour reactions of the dye itself and melting point determination with the original sample of dye.

Identification of residue II:

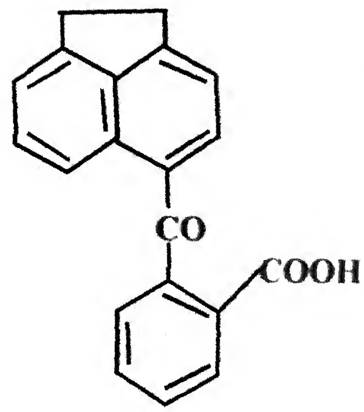
It was recrystallised from acetone (m.p.188-190^0 C). It gave positive tests for carboxyl group and was identified and confirmed as 2-(5'-chloro-2'chloromethylbenzoyl) benzoic acid by mixed melting point determination and superimposition of IR spectra with that of the authentic sample.

Identification of residue III:

The purified residue melted at 109-110^0 C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, Tollen's reagent and fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol. It was further confirmed by mixed melting point determination with the authentic sample of resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in chart E (chapter II).

DYES DERIVED FROM (3' ACENAPHTHOYL) BENZOIC ACID



A.1 Preparation of 2-(3'- acenaphthoyl) benzoic acid:

The acid was prepared by carrying out Friedel-Crafts reaction between acenaphthene (15.5g) and phthalic anhydride (19.5g, 0.1mole) with anhydrous aluminium chloride (27g, 0.2mole) used as a catalyst, nitrobenzene has been used as solvent. The reaction was carried out in a one liter three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 35 degree centigrade by adding anhydrous aluminium chloride in instalments. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until the evaporation of hydrogen chloride ceased. The mass was subjected to steam distillation to distill off the excess of nitrobenzene.

The heavy dark coloured complex was decomposed by adding 30 ml of concentrated hydrochloric acid (in 250 ml ice cold water). The residue was extracted three four times with boiling 10% solution of Na_2CO_3 and filtered. The acid was precipitated from the filtrate by the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and crystallized from acetone. The white crystalline acid has m.p. 199-201^{0}C, yield 15g. It is soluble in ether, ethanol, chloroform sparingly soluble in benzene and insoluble in CS_2.

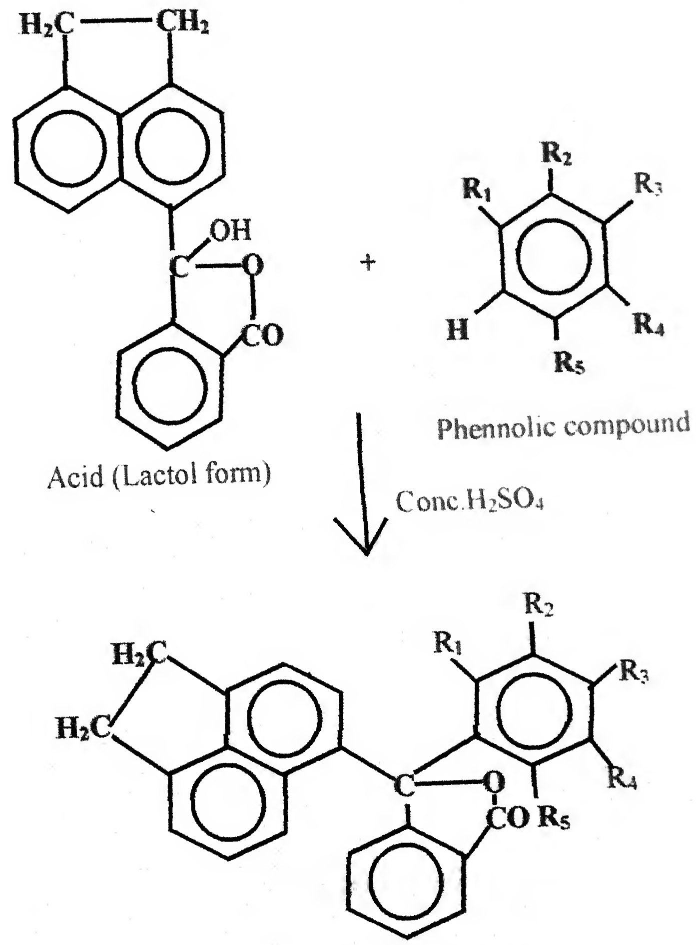
Anal.for.	:$C_{20}H_{14}O_3$ (mol. wt. 302)
Calc.	: C, 79.47; H, 4.63;
Found	:C, 79.28; H,4.55;

14.1 *Preparation of acetyl derivative:*

The acid (1.2g) and fused sodium acetate (3.5g) were refluxed with 20 ml of freshly distilled acetic anhydride at 130-140°C for four hours. The hot contents were poured into a beaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of brown coloured solid mass. The coloured acid derivative was decolourized by treatment with animal charcoal .It was crystallized from acetone in the form of amorphous solid, m.p. 171-173°C .It is soluble in acetone, chloroform and acetic acid, yield 0.75 g.

Anal.for : $C_{20}H_{13}O_3(COCH_3)$ (mol. wt. 344)
Calc. : C, 76.74; H, 4.65; acetyl, 12.5;
Found : C, 76.60; H, 4.59; acetyl, 12.42;

The dye prepared from the acid may be represented by the following structures.



Dye molecule

A 4.2 (3-acenaphyl)phenol phthal-as-ein
$R_1 = R_2 = R_4 = R_5 = H$, $R_3 = OH$

A 4.3 (3-acenaphyl) resorcinol phthal-as-ein
$R_2 = R_4 = R_5 = H$, $R_1 = R_3 = OH$

A 4.4 (3-acenaphyl) catechol phthal-as-ein
$R_3 = R_4 = R_5 = H$, $R_1 = R_2 = OH$

A 4.5 (3-acenaphyl) hydroquinone phthal-as-ein
$R_2 = R_3 = R_5 = H$, $R_1 = R_4 = OH$

A 4.6 (3-acenaphyl) pyrogallol phthal-as-ein
$R_4 = R_5 = H$, $R_1 = R_2 = R_3 = OH$

A 4.7 (3-acenaphyl) phloroglucinol phthal-as-ein
$R_2 = R_4 = H$, $R_1 = R_3 = R_5 = OH$

A 4.8 (3-acenaphyl) diacetyl resorcinol phthal-as-ein
$R_2 = R_4 = R_5 = H$, $R_1 = R_3 = OCOCH_3$

A 4.9 (3-acenaphyl) dibromo resorcinol phthal-as-ein
$R_5 = H$, $R_1 = R_3 = OH$, $R_2 = R_4 = Br$

A.4.2 Preparation of (3- acenapthyl) – phenol-phthal-as-ein:

The acid (1.5g) and phenol (1.0g) were condensed in an oil bath in presence of 4-5 drops of concentrated sulphuric acid at 180-190^{0}C for about four and a half hours till the molten mass of the tube became brittle on cooling. The condensed mass was taken out from the coloured tube and subjected to steam distillation to remove excess of phenol. The buff coloured solid mass left in the flask was powdered and extracted with 2% NaOH solution. It was filtered and the dye was precipitated from filtrate by the gradual addition of hydrochloric acid with constant stirring. It was purified by repeated crystallization from rectified spirit and dried in a vacuum desiccator, yield 1.3g.

The purity of the dye was tested by paper chromatography.

Paper	Whatman No 1
Mobil phase	Butanol saturated with ammonia

Developing agent 1% aqueous caustic soda.

Reference dye Phenolphthalein

A 25- cm x 10- cm was taken and a very dilute solution of the dye was spotted on the paper (on a base line 4.0 cm from the end) with a micro syringe. Similarly, a dilute aqueous solution of the reference dye was also spotted on the base line about 3.0 cm from the first spot. The mobile phase was allowed to run for thirteen hours. The paper was then taken out, dried and sprayed. Chromatogram of each dye gave only one corresponding spot. This confirmed the homogeneity and purity of the dye.

Found: R_f (phenolphthalein): 0.93

R_f [(3-acenaphthyl phenyl) phenol phthal-as-ein]: 0.94

Reported: R_f (phenolphthalein): 0.92

The grey coloured micro-crystalline dye, m.p. 110-112^{0}C gives light yellow colour in ethanol which turns into pink on adding a drop of an alkali. It is soluble in benzene, acetone and ethanol.

Anal.for :$C_{26}H_{18}O_3$ (mol. wt. 378)

Calc. :C, 82.53; H,4.76;

Found :C, 82.36; H4.73;

A. 4.3 Preparation of (3- acenaphthyl)-resorcinol-phthal-as-ein:

It was prepared by condensing an intimate mixture of the acid (3.0g) and resorcinol (3.0g) in the oil bath in presence of 4-5 drops of concentrated sulphuric acid at 150-160^{0}C for about four and half hours till the molten mass became hard and brittle on cooling. The condensed mass was crushed and washed with excess of water to remove excess of resorcinol. It was extracted with 2% aqueous solution of caustic soda and filtered. The dye was precipitated from reddish brown with green fluorescent filtrate by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 90^{0}C and then in a vacuum desiccator, yield 4.5g.

The red microcrystalline dye having m.p. 309-311^{0}C, is soluble in benzene,

ethanol, methanol and acetic acid. Its ethanolic solution is yellow which alters to yellowish orange with green fluorescence on adding a drop of an alkali. In strong basic medium, yellowish orange colour with intense green fluorescence in obtained.

Anal.for :$C_{26}H_{18}O_4$ (mol. wt. 394)

Calc. :C, 79.18; H,4.56;

Found :C, 79.02; H, 4.51;

A. 4.4 Preparation of (3- acenaphthyl)-catechol-phthal-as-ein:

The dye was prepared by heating a homogeneous mixture of the acid (1.2g) and catechol (1.5g) in an oil bath at 120-130^{0}C in presence of 4-5 drops of concentrated sulphuric acid for about four hours. The isolation and purification of the dye were done as in the case of (3- acenaphthyl phenyl) resorcinol phthal-as-ein. Yield 1.6g. The dye is dark brown in colour, m.p. above 300^{0}C. Its ethanolic solution is brown in colour. It gives bluish green colour on addition of alkali. It is soluble in acetone, ethanol and acetic acid.

Anal.for :$C_{26}H_{18}O_4$ (mol. wt. 394)

Calc. :C, 79.18; H,4.56;

Found :C, 79.04; H, 4.50;

A.4.5 Preparation of (3- acenaphthyl) hydroquinone phthal-as-ein:

It was prepared by condensing a homogeneous mixture of the acid (1.5g) and hydroquinone (1.5g). The intimate mixture was heated on oil bath at 160-170^{0}C in presence of 8-10 drops of concentrated sulphuric acid for about four hours till the molten mass became hard and brittle on cooling. The isolation and purification of the dye were done as in the case of (3- acenaphthyl phenyl) resorcinol phthal-as-ein. Yield 1.8 g.

The dark brown dye having m.p. above 360^{0}C, is soluble in chloroform, ethanol and methanol. Its alcoholic solution gives a reddish brown colour that turns into purple on addition of an alkali.

Anal.for :$C_{26}H_{18}O_4$ (molecular weight 394)

Calc. :C, 79.18; H,4.56;

Found :C, 79.00; H, 4.48;

A. 4.6 Preparation of (3- acenaphthyl) pyrogallol phthal-as-ein:

The mixture of the acid (1.0g), and pyrogallol (1.2g) was heated in the oil bath in presence of 6-8 drops of concentrated sulphuric acid at 140-160^{0}C for about four hours. The dye was isolated and purified in a manner similar to the other dyes, yield 1.2g.

The black shining crystals having a m.p. 205-207^{0}C, is soluble in ethanol, methanol and acetic acid. It dissolves in ethanol yielding reddish brown colour which turns violet on addition of a drop of an alkali.

Anal.for :$C_{26}H_{18}O_5$ (mol. wt. 410)

Calc. : C, 76.09 H, 4.39;

Found : C, 75.86 H, 4.34;

A. 4.7 Preparation of (3- acenaphthyl) phloroglucinol phthal-as-ein:

It was prepared by condensing a homogeneous mixture of the acid (1.2g) and phloroglucinol (1.5g). The intimate mixture was heated on oil bath at 180-200^{0}C for about four hours. The dye was isolated and purified in a manner similar to the other dyes, yield 1.0g.

The light brown dye m.p. 245^{0}C decomposed, gives light brown colour with ethanol, which turns into dark brown on adding a drop of an alkali. It is soluble in acetone, ethanol methanol and acetic acid.

Anal.for :$C_{26}H_{18}O_5$ (mol. wt. 410)

Calc. : C, 76.09; H,4.39;

Found : C, 75.80; H, 4.36;

A.4.8 Preparation of (3- acenaphthyl) diacetyl resorcinol phthal-as-ein:

[Acetylation of (3-acenaphthyl) resorcinol phthal-as-ein]

The dye (3-acenaphthyl phenyl) resorcinol phthal-as-a-ein (1.0g) and fused sodium acetate (3.0g) with 15.0ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The contents were refluxed at 130-140^{0}C for about four hours. The hot contents were poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon the light yellow solid settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallized from aqueous ethanol and a little acetic acid. It was dried in an oven at 80^{0}C and then over phosphorus pentoxide under reduced pressure, yields 0.65g.

The crystalline acetyl derivative is yellowish white coloured and has a m.p. 146-148^{0}C. It is soluble in ethanol, acetone and acetic acid.

Anal.for :$C_{26}H_{16}O_4$ ($COCH_3$) (mol. wt. 478)

Calc. : C, 75.31; H, 4.60; Acetyl, 18.02;

Found : C, 75.18; H, 4.58; Acetyl, 17.92;

A. 4.9 Bromination of (3- acenaphthyl) resorcinol phthal-as-ein:

[(3-acenaphthyl) dibromo resorcinol phtha-as-ein]

The dye (3-acenaphthyl)-resorcinol-phthal-as-ein (1.0g) was dissolved in minimum quantity of glacial acetic and 15 ml of a 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130^{0}C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dirty orange powder settled down. It was filtered and washed well with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The brominated dye was finally purified by crystallization from aqueous ethanol and dried at 80^{0}C in an oven and then in a vacuum desiccator, yield, 1.2g.

The brick red crystalline compound having m.p. 134-136^{0}C is soluble in benzene, ether, chloroform, acetone and acetic acid. Its ethanolic solution is yellow in colour which turns into yellowish orange with green fluorescence on adding a drop of alkali.

Anal.for :$C_{26}H_{16}Br_2O_4$ (mol. wt. 552)

Calc. : Br, 28.98;

Found : Br, 28.82;

A.4.10 Caustic potash treatament of (3- acenaphthyl) resorcinol phthal-as-ein:

Potassium hydroxide pellets (10.0g) were taken in a crucible and heated with a few drops of water to make a paste. The dye (1.0) was then added to it. The contents were heated for about four hours till the darkened colour of the dye faded completely. After cooling, the contents were diluted with 50 ml of water and filtered. The dark residue (I) settled down on just neutralizing the alkali. It was filtered and washed well with water. The filtrate, when acidified further by adding excess of dilute hydrochloric acid gave white precipitate (II), which was filtered and washed with water. It was crystallized from aqueous ethanol and dried in a vacuum desiccator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Residue- I

It was identified and confirmed to be the unreacted dye from its colour reaction and determination of the mixed melting point with the authentic sample.

Residue –II

It was acidic in nature and gave positive tests for the presence of carboxylic group. It was identified as 2-(3'acenaphthoyl) benzoic acid and confirmed by mixed melting point determination (m.p. 199-201^{0}C) and by superimposition of the IR spectra of the authentic sample.

Residue-III

The purified sample melted at 109-110^{0}C. It gave positive testes with Ferric chloride, Fehling's solution and ammonical silver nitrate. It gave fluorescein test with phthalic anhydride. On the basis of these observation, it was confirmed to be resorcinol. Acetylation, bromination and caustic potash treatment of the dye are shown in chart G in Chapter II.

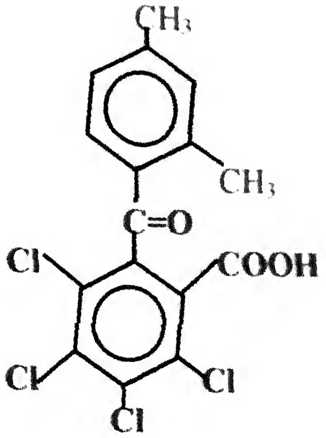
CHAPTER

FOUR

EXPERIMENTAL-B

CHAPTER IV

DYES DERIVED FROM 2-(2' 4'- DIMETHYL BENZOYL) TETRACHLORO BENZOIC ACID :



B.1 Preparation of 2-(2' 4' dimethyl-benzoyl) tetrachloro benzoic acid.

The acid was prepared by carrying out Friedel-Crafts reaction between dry AR 80ml of meta-xylene and 28.0 g of tetrachloro phthalic anhydride in presence of anhydrous aluminium chloride (27.0g) as a catalyst, in a similar manner as 2-(2' 4' demthyl benzoyl) benzoic acid chapter III. The yield of the acid obtained was 14.0g. The crude acid was crystallised from methanol in the form of yellow crystals, m.p. 220-222^{0}C. The acid is soluble in water, ether and methanol.

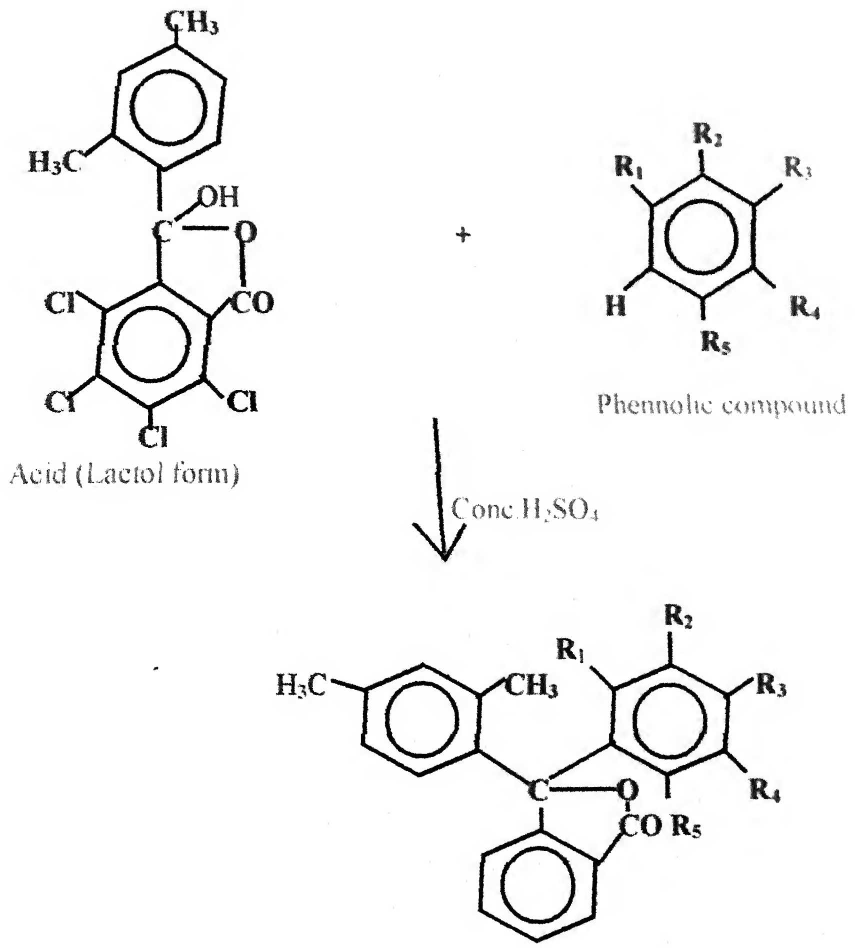
Anal. For	: $C_{16}H_{10}Cl_4O_3$ (mol. Wt. 392)
Calc	: C, 48.98; H, 2.55; Cl,36.22;
Found	: C, 48.80; H, 2.50; C, 36.14;

B. 1.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

It was prepared and purified in a manner similar to that described under acetylation of 2-(2' 4' dimethyl benzoyl) benzoic acid (A 1.1 chapter III). The light brown coloured acetylated product soluble in acetone and choroform has m.p. 122^{0}C.

Anal. For	: $C_{18}H_{12}Cl_4O_4$ or $C_{16}H_9Cl_4O_3$ ($COCH_3$) (mol. Wt. 434)
Calc	: C, 49.77; H, 2.76; Cl,32.72; acetyl, 9.91;
Found	: C, 49.59; H, 2.70; C, 32.60; acetyl, 9.87;

The dyes prepared from the acid may be represented by the following general formula.



Dye molecule

B.1.2 (2, 4- dimethyl phenyl) phenol tetrachloro phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = H; R_3 = OH$

B.1.3 (2,4- dimethyl phenyl) resorcinol tetrachloro phthal-as-ein.

$R_2 = R_4 = R_5 = H; R_1 = R_3 = OH$

B.1.4 (2,4- dimethyl phenyl) catechol tetrachloro phthal-as-ein.

$R_3 = R_4 = R_5 = H; R_1 = R_2 = OH$

B.1.5 (2,4- dimethyl phenyl) hydroquinone tetrachloro phthal-as-ein.

$R_2 = R_3 = R_5 = H; R_1 = R_4 = OH$

B.1.6 (2,4- dimethyl phenyl) pyrogallol tetrachloro phthal-as-ein.

$R_4 = R_5 = H; R_2 = R_2 = R_3 = OH$

B.1.7 (2,4- dimethyl phenyl) phyloroglucinol tetrachloro phthal-as-ein.

$R_2 = R_4 = H; R_1 = R_3 = R_5 = OH$

B.1.8 (2,4- dimethyl phenyl) diacetyl resorcinol tetrachloro phthal-as-ein.

$R_2 = R_4 = R_5 = H; R_1 = R_3 = OCOCH_3$

B.1.9 (2,4- dimethyl phenyl) dibromo resorcinol tetrachloro phthal-as-ein.

$R_5 = H; R_1 = R_3 = OH; \; R_2 = R_4 = Br$

B1.2 PREPARATION OF (2,4-DIMETHYL PHENYL) PHENOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by condensing the homogeneous mixture of the acid (2.0 g) and phenol (1.0 g) at 160-170^{0}C for four hours in presence of few drops concentrated sulphuric acid. The dye was isolated and purified similarly as described in the case of (2, 4 dimethyl phenyl) phenol phthal-as-ein (A.1.2 chapter III), yield 1.82g.

The pink coloured dye has m.p. 230-232^{0}C. Its ethanolic solution is wine red coloured which turns into violet on addition a drop of alkali.

Anal. For	: $C_{22}H_{14}Cl_4O_3$ (mol. Wt. 468)
Calc	: C, 56.41; H, 2.99; Cl,30.34;
Found	: C, 56.32; H, 2.96; C, 30.28;

B.1.3 PREPARATION OF (2,4-DIEMTHYL PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

It was prepared by heating the intimate mixture of the acid (5.2g) and resorcinol (3.0g) in an oil bath at 140-160^{0}C in presence of sulphuric acid (concentrated 6-8 drops) for about four and half hours. The isolation and purification of the dye were carried out in a manner similar to that described in the case of (A.1.3 chapter III), yield 4.8g.

The golden brown coloured dye, m.p. 280-282^{0}C gives pale cremal colour in ethanol which turns into pinkish orange with green fluorescence on adding a drop of alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal. For	: $C_{22}H_{14}Cl_4O_4$ (mol. Wt. 484)
Calc	: C, 56.55; H, 2.89; Cl,29.34;
Found	: C, 54.40; H, 2.86; C, 29.26;

B.1.4 PREPARATION OF (2, 4 DIMETHYL PHENYL) CATECHOL TETRACHLORO PHTHATL-AS-EIN :

Condensation of the acid (2.0g) and catechol (1.5g) was carried out at 120-140^{0}C for four hours by using 3-4 drops of concentrated sulphuric acid as condensing agent. The dye was isolated and purified exactly in a similar manner as the other dyes. The black coloured dye, m.p. 248-250^{0}C gives brown colour in ethanol which is not changed on addition of alkali.

Anal. For	: $C_{22}H_{14}Cl_4O_4$ (mol. Wt. 484)
Calc	: C, 54.55; H, 2.89; Cl,29.34;
Found	: C, 54.35; H, 2.86; C, 29.26;

B. 1.5 PREPARATION OF (2,4 DIMETHYL PHENYL) HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN :

An intimate mixture of acid (1.5g) and hydroquinone (1.0g) was heated in an

oil bath 160-170^{0}C, in presence of concentrated sulphuric acid (3-4 drops). The reaction, isolation and the purification were carried out in a manner similar to (B.1.3), yield 1.3g m.p. 320^{0}C (decomposed).

The light black dye, soluble in ethanol gives golden brown colour which is not changed on adding a drop of alkali. It gives dark brown colour in strong basic medium.

Anal. For	: $C_{22}H_{14}Cl_4O_4$ (mol. Wt. 484)
Calc	: C, 54.55; H, 2.89; Cl,29.34;
Found	: C, 54.40; H, 2.83; C, 29.22;

B.1.6 PREAPARATION OF (2,4 DIMETHYL PHENYL) PYROGALLOL TETRACHLORO PHTHAL-AS-EIN :

The dye was prepared by condensing the acid (2.0g) and pyrogallol (1.4g) by using 2-3 drops of conc. sulphuric acid as condensing agent. Heating was continued for four hours at 130-145^{0}C, till brittle mass was obtained on cooling. Isolation and purification were done in same way as in case of (2, 4 dimethyl phenyl) resorcinol tetrachloro phthal-as-ein, yield 1.8g.

The blackish brown dye having m.p. above 360^{0}C, is soluble in acetone, ethanol, methanol and acetic acid. It gives golden brown and brown colour in ethanol and alcoholic caustic potash solution respectively.

Anal. For	: $C_{22}H_{14}Cl_4O_5$ (mol. Wt. 500)
Calc	: C, 52.80; H, 2.80; Cl,28.40;
Found	: C, 52.61; H, 2.76; C, 28.30;

B.1.7 PREAPARAION OF (2,4 DIMETHYL PHENYL) PHLOROGLUCINOL TETRACHLORO PHTHAL-AS-EIN :

The mixture of acid (1.5g) phloroglucinol (1.5g) and few drops(6-8) concentrated sulphuric acid was heated in an oil bath at 190-200^0 C for three and half hours . The dye was isolated and purified exactly as B 1.3 yield 3.0g. The dark orange dye having m.p.248^0 C (decomposed), gives wine red colour in ethanol which turns into dark red on adding a drop of alkali.

Anal. For : $C_{22}H_{14}Cl_4O_5$ (mol. Wt. 500)

Calc : C, 52.80; H, 2.80; Cl,28.40;

Found : C, 52.60; H, 2.73; Cl, 28.24;

B.1.8 ACETYLATION OF (2,4-DIMETHYL PHENYL) RESORCINOL TETRECHLORO PHTHAL -AS- EIN:

PREPARATION OF (2,4-DIMETHYL PHENYL) DIACETYL RESORCINOL TETRACHIORO PHTHAL-AS-EIN:

Acetylation and isolation of the acetylderivative was carried out as in case of A.1.8 chapter III, yield 0.80g.

The buff coloured diacetyl derivative having m.p. 314-316^0 C is soluble in benzene, chloroform and acetic acid.

Anal. For : $C_{26}H_{18}Cl_4O_6$ or $C_{22}H_{12}Cl_4O_4(COCH_3)_2$ (mol. Wt. 568)

Calc : C, 54.93; H, 3.17; Cl,25.00; acetyl,15.14;

Found : C, 54.73; H, 3.13; Cl, 24.93 acetyl, 15.08;

B.1.9 BROMINATION OF (2,4 DIMETHYL PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

PREPARATION OF (2,4 DIMETHYL PHENYL) DIBROMO RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

The dye resorcinol (1.0g) was dissolved in a minimum quantity of glacical acetic acid and 10ml of 10% solution of bromine in glacial acetic acid was slowly added in the solution of dye. The flask was fitted with an air condenser and the contents were refluxed at 120^0 C for an hour. The extraction and purification of the brominated compound were done as in the case of bromination of (2,4 dimethyl phenyl) resorcinol phthal-as-ein (A.1.9 chapter III), yield 0.90g.

The pale yellow coloured dye having m.p. 119-120^0 C is soluble in ether, methanol, acetone and chloroform.

Anal. For : $C_{22}H_{12}Cl_4O_4Br_2$ (mol. Wt. 642)

Calc : Br, 24.92;

Found : Br, 24.75;

B.1.10 CAUSTIC POTASH TREATMENT OF (2, 4 DIMETHYL PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

Caustic potash fusion of the dye (1.0g) was carried out exactly in a similar manner as described in the case of (2, 4 dimethyl phenyl) resorcinol phthal-as-ein (A.1.10 chapter III), yielding following three residues:

Identification of residue (I) :

Residue (I) was identified as unreacted residual dye from its colour reactions. It was further confirmed by mixed melting point determination with the original dye.

Identification of Residue (II) :

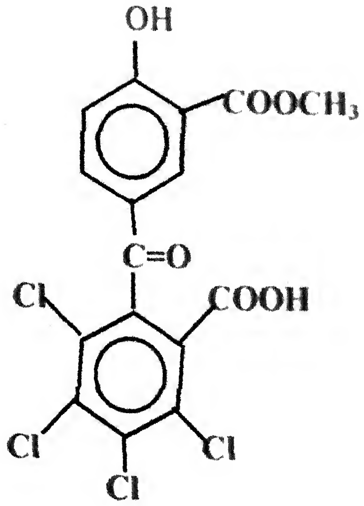
It was found to be acidic in nature and gave positive test for carboxylic group and was indentified as 2- (2' 4' dimethyl benzoyl) tetra chloro benzoic acid and confirmed by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Identification of Residue (III) :

The purified substance (III) melted at 109-110^0 C. It gave violet blue colour with ferric chloride, reduced Fehling's solution and Tollen's reagent. It responded to fluorescein test with phthalic anhydride. On the basis of these observations the residue III was identified as resorcinol. It was further confirmed by mixed melting point determination with the authentic sample.

The acetylation, bromination and caustic potash treatment of the dye are shown in chart A, chapter II.

DYES DERIVED FROM 2-(3'- CARBMETHOXY 4'- HYDROXY BENZOYL) TETRACHLORO BENZOIC ACID:



B. 2. PREPARATION OF 2-(3'-CARBMETHOXY 4'-HYDROXY BENZOYL) TETRACHLORO BENZOIC ACID :

The acid was prepared by carrying out Friedel- Crafts reaction between methyl, salicylate (dry AR 80ml) and tetrachloro phthalic anhydride (28.5g about 0.1mole) in presence of anhydrous aluminium chloride (27g about 0.2 mole) as catalyst. The reaction and isolation were carried out in a similar manner as in the case of 2-(3'-carbmethoxy 4'-hydroxy benzoyl) benzoic acid (A.2 chapter III) yield 20g. The crude acid was crystallized from methanol in the form of cream coloured crystals. m.p. 220^0 C (decomposed). It is soluble in hot water, ether and methanol.

Anal. For.	: $C_{16}H_8Cl_4O_6$	(mol.wt. 438)
Calc	: C, 43.84; H,1.83; Cl, 32.42;	
Found	: C, 43.65; H, 1.81; Cl, 32.33;	

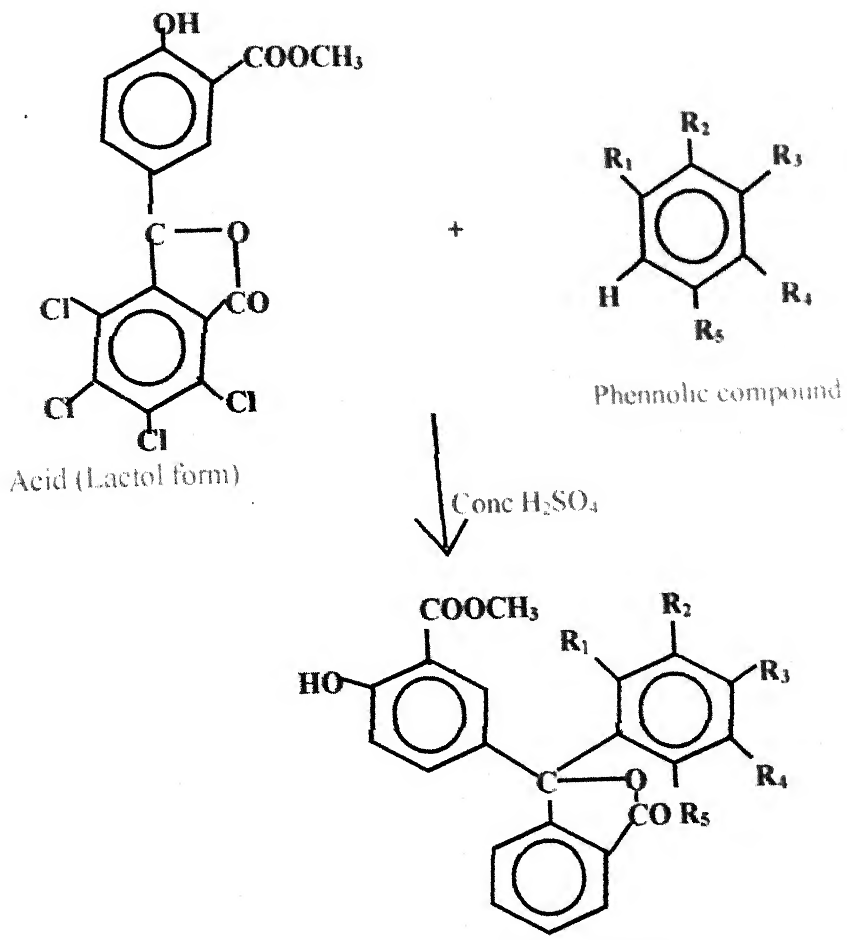
B. 2.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

The acid (1.0g) and fused sodium acetate (3.0g) were refluxed with 15ml of freshly distilled acetic anhydride exactly in a similar manner as (A.1.1 chapter III). The brown coloured acetyl derivative having m.p. $207\text{-}209^0$ C is soluble in chloroform, acetone and acetic acid.

Anal. For. : $C_{20}H_{12}Cl_4O_8$ or $C_{16}H_6Cl_4O_6$ $(COCH_3)_2$ (mol.wt. 522)

Calc : C, 43.84; H,1.83; Cl, 32.42;

Found : C, 43.65; H, 1.81; Cl, 32.33;



Dye molecule

B.2.2 (3-carbmethoxy 4-hydroxy phenyl) phenol tetrachloro phthal-as-ein.

$R_1=R_2=R_4=R_5=H$; $R_3=OH$

B.2.3 (3-carbmethoxy 4-hydroxy phenyl) resorcinol tetrachloro phthal-as-ein.

$R_2=R_4=R_5=H$; $R_1=R_3=OH$

B.2.4 (3-carbmethoxy 4-hydroxy phenyl) catechol tetrachloro phthal-as-ein.

$R_3=R_4=R_5=H$; $R_1=R_2=OH$

B.2.5 (3-carbmethoxy 4-hydroxy phenyl) hydroquinone tetra chloro phthal-as-ein.

$R_2=R_3=R_5=H$; $R_1=R_4=OH$

B.2.6 (3-carbmethoxy 4-hydroxy phenyl) pyrogallol tetra chloro phthal-as-ein

$R_4=R_5=H$; ; $R_1=R_2=R_3=OH$

B.2.7 (3-carbmethoxy 4-hydroxy phenyl) phloroglucinol tetra chloro phthal-as-ein

$R_2=R_4=H$; $R_1=R_3=R_5=OH$

acetoxy
B.2.8 (3-carbmethoxy 4-~~hydroxy~~ phenyl) diacetyl resorcinol tetrachloro phthal-as-ein.

$R_2=R_4=R_5=H$; $R_1=R_3=OCOCH_3$

B.2.9 (3-bromo 5-carbmethoxy 4-hydroxy phenyl) dibromo resorcinol tetrachloro phthal-as-ein.

$R_5=H$; $R_1=R_3=OH$;$R_2=R_4=Br$

B.2.2 PREPARTION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) PHENOL TETRACHLORO PHTHAL- AS-EIN:

The dye was prepared by condensing the acid (2.0g) and phenol (1.0g) in presence of 3-4 drops of conc. sulphuric acid. The heating, isolationand purification were carried out exactly in a similar manner as in case of (3-carbmethoxy 4-hydroxy phenyl) phenol phthal-as-ein (A.1.2 chapter III), yield 1.6g. The orange dye having m.p 240-242^0 C gives golden yellow colour with ethanol, which turns into violet on adding a drop of alkali.

Anal.for : $C_{22}H_{12}Cl_4O_6$ (Mol.Wt 514)

Calc. : C,51.36; H,2.33; Cl, 27.63;

Found : C, 51.20; H, 2.3; Cl, 27.57;

B.2.3. PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

It was prepared by heating the homogenous mixture of the acid (3.0g) and resorcinol (3.0g) in an oil bath at 140-160^0 C. The concentrated sulphuric acid (4-6 drops) was used as a condensing agent. The heating was continued for about four hours. Isolation and purification of the dye were carried out in a similar manner as in the case of (A.2.3 chapter III) yield 2.5g.

The light brown shining dye having m.p.280-282^0 C, gives pale yellow colour with ethanol, which turns into reddish orange with green fluorescence on adding a drop of alkali. It is soluble in benzene and acetic acid.

Anal. For. : $C_{22}H_{12}Cl_4O_7$ (Mol. W.t. 530)

Calc. : C,49.81 ; H, 2.26 ; Cl 26.79 ;

Found : C, 49.65; H, 2.23 ; Cl, 26.70;

B.2.4. PREPARTION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) CATECHOL TETRACHLORO PHTHL-AS-EIN :

The condensation of the intimate mixture of acid (1.5g) and catechol (1.5g) was carried out in presence of 4-6 drops of conc. Sulphuric acid at 120-130^0 C for about four hours. Isolation and purification were carried as in the case of (A.2.3 CHAPTER III) yield 1.6g.The light black coloured, dye having m.p. 240-241^{0}C, gives brown colour with ethanol, which turns into blackish-brown on adding a drop of alkali.

Anal. For : $C_{22}H_{12}Cl_4O_7$ (Mol.wt 530)

Calc. : C,49.81, H, 2.26 ; Cl, 26.79;

Found : C, 49.64; H, 2.24 ; Cl, 26.65;

B.2.5 PREPARTION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN :

The mixture of acid (1.5g) hydroquinone (1.5g) and 3-4 drops of concentrated sulphuric acid, was heated in an oil bath at 160-180^0 C, for about four hours. The isolation purification of the dye were done as described in the case of

(A.2.3. chapter III), yield 1.62g. The black dye having m.p 300^0 C (decomposed), gives light brown colour with ethanol, which turns into dark brown on adding a drop of alkali.

Anal. For : $C_{22}H_{12}Cl_4O_7$ (Mol.wt 530)

Calc. : C,49.81, H, 2.26 ; Cl, 26.79;

Found : C, 49.74; H, 2.24 ; Cl, 26.64;

B.2.6 PREPARTION (3-CARBMETHOXY 4-HYDROXY PHENYL) PYROGALLOL TETRACHLORO PHTHAL-AS-EIN:

The mixture of acid (1.5g) pyrogallol (1.5g) and concentrated sulphuric acid (3-5 drops) was heated in an oil bath at 130-140 ^{0} C for about three and half hours. The isolation and purification were carried out in a same manner as (A.2.3 chapter III), yield 1.5g.

The dye is brown in colour, m.p. above 360^0 C. It shows wine red colour in ethanol which turns into blue colour on adding a drop of alkali.

Anal. For : $C_{22}H_{12}Cl_4O_8$ (Mol.wt 546)

Calc. : C,48.35, H, 2.20 ; Cl, 26.00;

Found : C, 48.16; H, 2.18 ; Cl, 25.95;

B.2.7. PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) PHLOROGLUCINOL TETRACHLORO PHTHAL-AS-EIN :

The condensation of the intimate mixture of acid (1.5g), phloroglucinol (1.5g) was carried out in presence of 3-4 drops of conc. Sulphuric acid at 190-200^0 C for four hours. Isolation and purification of the dye were done as in the case of A.2.3. chapter III , yield 1.8g.

The dark orange dye decomposed above 300 ^{0} C. It gives wine red colour with ethanol, with turns into red with green fluorescence on adding a drop alkali.

Anal. For : $C_{22}H_{12}Cl_4O_8$ (Mol.wt 546)

Calc. : C,48.35, H, 2.20 ; Cl, 26.00;

Found : C, 48.20; H, 2.17 ; Cl, 25.92;

B.2.8 PREPARATION OF (4-ACETOXY 3-CARBMETHOXY PHENYL) DIACETYL RESORCINOL TETRACHLORO PHTHAL-AS-EIN

Acetylation of (3-carbmethoxy 4-hydroxy phenyl) resorcinol tetrachloro phthal-as-ein

The dye, (3-carbmethoxy 4-hydroxy phenyl) resorcinol tetrachloro phthal-as-ein (1.0g), fused sodium acetate (3.0g) and freshly distilled acetic anhydride (15ml), were taken in a 50ml round bottom flask fitted with an air condenser. The reaction, isolation and purification were carried out in a similar manner as in the case of A.2.8 chapter III, yield 0.75g.

The golden brown coloured triacetyl derivative dye having m.p. 166-168 ^{0} C, is soluble in benzene, solv. Ether, chloroform and acetic acid.

Anal. For : $C_{28}H_{18}Cl_4O_{10}$ or $C_{22}H_9Cl_4O_7(COCH_3)_3$ (Mol. Wt. 656)

Calc. : C, 51.22; H, 2.74 ;Cl, 21.65 ; acetyl, 19.66 ;

Found : C, 51.03; H, 2.71; Cl, 21.50; acetyl, 19.60;

B.2.9 BROMINATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

The resorcinol (1.0g) was dissolved in a minimum quantity of glacial acetic acid, was slowly added in the solution of dye. The reaction, isolation and purification were carried out in a similar manner as in case A.2.9 chapter III, yield 0.80g.

The pale yellow micro crystalline dye having m.p 308-309^{0} C, is soluble in solvent ether, alcohol, chloroform and acetic acid.

Anal. For : $C_{22}H_9Cl_4Br_3O_7$ (Mol.wt 767)

Calc. : Br, 31.29; Found : Br, 31.20;

B.2.10 CAUSTIC POTASH TREATMENT OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

Caustic potash treatment of the dye (1.0g) was carried out exactly in a

similar manner as in case of (A.2.10 chapter III), as a result following three residues were obtained.

Identification of residue (I):

It was identified as unreacted residual dye on the basis of its colour reactions and confirmed by mixed melting point determination with authentic sample.

Identification of residue (II):

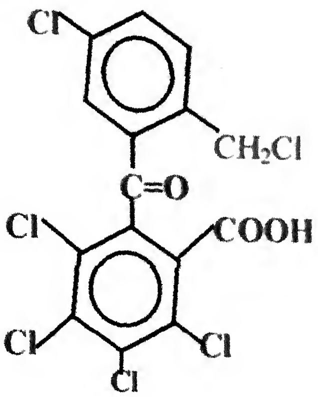
It gives positive test for carboxyl and phenolic groups and was identified and confirmed as 2-(3'-carbmethoxy 4'-hydroxy benzoyl) tetrachloro benzoic acid by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Identification of residue (III):

It was identified and confirmed as resorcinol because it gave violet colour with ferric chloride solution, reduced Tollen's reagent and Fehling's solution. It shows no depression in m.p. 108-109^0 C when mixed with the authentic resorcinol sample.

The acetylation bromination and caustic potash fusion of the dye are given in chart C (chapter II).

DYES DERIVED FROM 2-(5'-CHLORO-2'-CHLOROMETHYL BENZOYL) TETRACHLORO BENZOIC ACID :



2-(5'-chloro-2'- chloromethyl benzoyl) tetrachlorbenzoic acid

B.3 PREPARATION OF 2-(5'-CHLORO 2'-CHLOROMETHYL BENZOYL) TETRACHLORO BENZOIC ACID:

The acid was prepared by carrying out Friedel Crafts reaction between 4-chlorobenzyl chloride and tetrachloro phthalic anhydride and anhydrous $AlCl_3$. Starting with 4-chlorobenzylchloride (AR, dry 100 ml), along with tetrachloro phthalic anhydride (28.5g, 0.1 mole) and anhydrous aluminium chlororide (27.0g, about 0.2 mole) used as catalyst, the acid was prepared following the procedure outlined in subsection A. 3 chapter III for the preparation of 2-(5'-chloro 2'-chloromethyl benzoyl) benzoic acid

.

The acid was isolated as dirty white crystals which had a melting point of 258-260^0 C (dec.). The crystalline solid was found to be soluble in acetone chloroform and methanol, yield 15.5g.

Anal. : $C_{15}H_6Cl_6O_3$ (Mol. Wt.447)

Calc. : C. 40.27; H, 1.34; Cl, 47.65;

Found : C, 40.04; H, 1.32; Cl, 47.48;

B 3.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

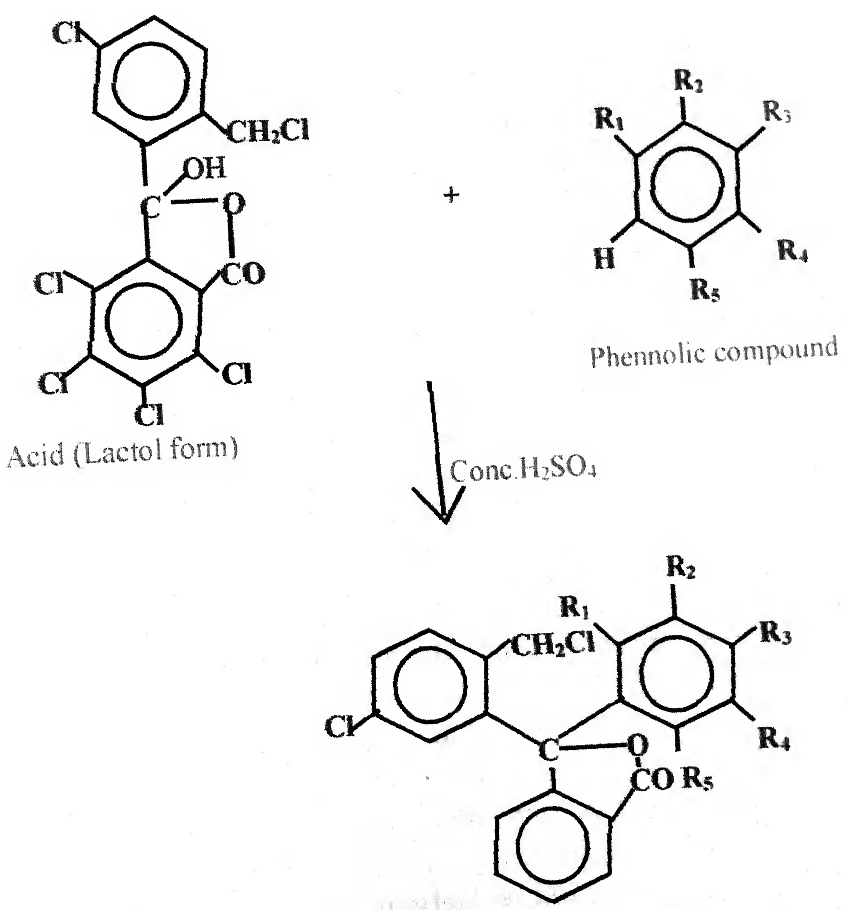
1.0g of the acid 3.0g of fused sodium acetate was refluxed with 15 ml of freshly distilled acetic anhydride at 120-130^0 C in the same way as done for 2-(5-' chloro 2'- chloromethyl benzoyl) benzoic acid described in A. 3.1 chapter III. It was crystallised from acetone in the form of a brown solid decomposing at 145-147^0 C. It is soluble in ethanol, benzene, chloroform and acetic acid yield 0.60g.

Anal. : $C_{17}H_8Cl_6O_4$ or $C_{15}H_5Cl_6O_3$(OC.CH_3 (Mol. Wt.489)

Calc. : C. 41.72; H, 1.64; Cl, 43.56; acetyl 8.79;

Found : C, 41.60; H, 1.60; Cl, 43.43; acetyl 8.76

The dyes prepared from the acid may be represented by the following structures:



Dye molecule

B.3.2 (5-chloro – 2-chloromethyl phenyl) phenol tetrachloro phthal-as –ein:
$R_1 = R_2 = R_4 = R_5 = H, R_3 = OH$

B.3.3 (5-chloro – 2-chloromethyl phenyl) resorcinol tetrachloro phthal-as –ein:
$R_2 = R_4 = R_5 = H, R_1 = R_3 = OH$

B.3.4 (5-chloro – 2-chloromethyl phenyl) catechol tetrachloro phthal-as –ein:
$R_3 = R_4 = R_5 = H, R_1 = R_2 = OH$

B.3.5 (5-chloro – 2-chloromethyl phenyl) hydroquinone tetrachloro phthal-as –ein:
$R_2 = R_3 = R_5 = H, R_1 = R_4 = OH$

B.3.6 (5-chloro – 2-chloromethyl phenyl) pyrogallol tetrachloro phthal-as –ein:
$R_4 = R_5 = H, R_1 = R_2 = R_3 = OH$

B.3.7 (5-chloro – 2-chloromethyl phenyl) phloroglucinol tetrachloro phthal-as –ein:
$R_2 = R_4 = H, R_1 = R_3 = R_5 = OH$

B.3.8 (5-chloro – 2-chloromethyl phenyl) diacetyl resorcinol tetrachloro phthal-as –ein:
$R_2 = R_4 = R_5 = H, R_1 = R_3 = O.CO.CH_3$

B.3.9 (5-chloro – 2-chloromethyl phenyl) dibromo resorcinol tetrachloro phthal-as –ein:
$R_5 = H, R_1 = R_2 = R_3 = R_4 = Br$

B.3.2 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) PHENOL TETRACHLORO PHTHAL-AS-EIN :

A homogenized intimate mixture of 2.0g of the acid and 1.5g of phenol was heated in a hard boiling tube to make it homogeneous. It was then condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-175^0 C for about four and half hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The reddish pink solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallization from rectified spirit and dried in vaccum desiccator, yield 1.40g. The purity of the dye was tested by paper chromatography as in case A.1.2 chapter III.

The pinkish white dye has a m.p. 248-250^0 C. It is soluble in ethanol, acetone, ether and acetic acid. The ethanolic solution of the dye is light yellow in colour that turns into rose red colour on adding a drop of an alkali.

Anal.	: $C_{21}H_{10}Cl_6O_3$	(Mol. Wt.523)
Calc.	: C. 48.18; H, 1.91; Cl, 40.73;	
Found	: C, 48.05; H, 1.90; Cl, 40.61;	

B. 3.3 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

It was prepared by the condensation of 3.0g of the acid and 2.5g of resorcinol (excess than the molecular proportion) on and oil bath in presence of 5-6 drops of concentrated sulphuric acid at 150-170^0 C for about four and half-hours. It was isolated and purified as described for A. 3.3 chapter III, yield 3.0g.

The golden yellow crystalline dye having a m.p. 296-298^0 C is soluble in acetic acid, ethanol and ether. It dissolves in ethanol giving a deep orange colour with green fluorescence with an alkali and pink colour with green fluorescence with alcoholic caustic potash solution.

Anal.	: $C_{21}H_{10}Cl_6O_4$	(Mol. Wt.539)
Calc.	: C. 46.75; H, 1.86; Cl, 39.52;	
Found	: C, 46.52; H, 1.80; Cl, 39.43;	

B.3.4 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) CATECHOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 1.0g each of the acid and catechol in an oil bath at 110^0 C to make it uniform and homogeneous. Then the intimate mixture was condensed for four and half hours in presence of a few drops of concentrated sulphuric acid. The isolation and the purification of the dye were done in a manner similar to that in the case of phenol phthal-as-ein described in A.3.2 chapter III, yield 1.5g.

The black crystalline dye having a m.p. 256-258^0 C is soluble in ethanol to yield a light brown colour in ethanol that turns to dark brown on adding a drop of an alkali.

Anal. : $C_{21}H_{10}Cl_6O_4$ (Mol. Wt.539)

Calc. : C. 46.75; H, 1.86; Cl, 39.52;

Found : C, 46.63; H, 1.80; Cl, 39.31;

B.3.5 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN:

1.5g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath at 160-180^0 C for three hours in presence of a few drops of concentrated sulphuric acid. The isolation and purification of the dye ws carried out in a manner similar to the one adopted for A. 3.3 chapter III, yield 1.2g.

The blackish brown dye, having m.p. above 360^0 C is soluble in ethanol giving a leaf brown colour that turns into brown on the addition of 2% caustic soda solution.

Anal. : $C_{21}H_{10}Cl_6O_4$ (Mol. Wt.539)

Calc. : C. 46.75; H, 1.86; Cl, 39.52;

Found : C, 46.62; H, 1.80; Cl, 39.38;

B.3.6 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) PYROGALLOL TETRACHLORO PHTHAL-AS-EIN:

The intimate and homogenized mixture of 1.5g of the acid and 1.0g of pyrogallol was condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 135-145^0 C for about three hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for A. 3.3 chapter III, Yield 0.70g.

The blackish brown coloured dye having m.p. above 360^0 C gives an ethanolic solution leaf brown in colour which on adding a drop of an alkali becomes violet.

Anal. : $C_{21}H_{10}Cl_6O_5$ (Mol. Wt.555)

Calc. : C. 45.41; H, 1.80; Cl, 38.38;

Found : C, 45.28; H, 1.76; Cl, 38.28;

B. 3.7 PREPARATION OF (5-CHLORO-2-CHLROMETHYLPHENYL) PHLOROGLUCINOL TETRACHLORO PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.5g of the acid and 1.0g of phloroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 200-220^0 C for about three hours. The isolation and purification of the dye was performed in the same way as that described for A.3.3 chapter III, yield 0.80g.

The blackish brown coloured dye m.p. 320^0 C (dec.) yields a golden brown coloured solution in ethanol that turns dark red on adding a drop of an alkali.

Anal. : $C_{21}H_{10}Cl_6O_5$ (Mol. Wt.555)

Calc. : C. 45.41; H, 1.80; Cl, 38.38;

Found : C, 45.30; H, 1.76; Cl, 38.26;

B.3.8 ACETYLATION OF (5-CHLORO-2-CHLORMETHYLPHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

[(5-CHLORO-2-CHLOROMETHYL PHENYL) DIACETYL RESORCINOL TETRACHLORO PHTHAL-AS-EIN]

1.0g of the 5-chloro-2-chloromethyl phenyl) resorcinol tetrachloro phthal-as-ein dye, 3.0g fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The acetylation, isolation and purification of acetylated product was carried out in exactly the same manner as in the case of A.3.8 chapter III, Yield 0.70g.

The buff coloured diacetly derivative (m.p. 160-162^0 C) ia soluble in benzene, carbon tetrachloric and chloroform.

Anal. : $C_{25}H_{14}Cl_6O_6$ or $C_{21}H_8Cl_6O_4(OC.CH_3)_2$ (Mol. Wt.623)

Calc. : C. 48.15; H, 2.25; Cl, 34.19; acetyl 13.80;

Found : C, 48.00; H, 2.20; Cl, 34.10; acetyl 13.73;

B.3.9 BROMINATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

[(5-CHLORO-2-CHLOROMETHYLPHENYL) DIBROMO RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

The 1.0g of the dye 5-chloro-2-chloromethyl phenyl resorcinol tetrachloro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10 ml of 10% solution of bromine in glacial acetic was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130^0 C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A blackish rose powder settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 110^0 C in an oven and then in a vacuum desiccator, yield 1.10g.

The blackish rose coloured powdery dye having m.p. 326-328^0 C is soluble in benzene, ethanol, and acetone.

Anal.	: $C_{21}H_8Cl_6Br_2O_4$ (Mol. Wt.697)
Calc.	: Br, 22.96;
Found	: Br,22.84;

B.3.10 CAUSTIC POTASH TREATMENT OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

10.0g of Potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to carry out the caustic potash treatment exactly in the same way as described in A. 3.10 chapter III.

Identification of residue I :

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of residue II :

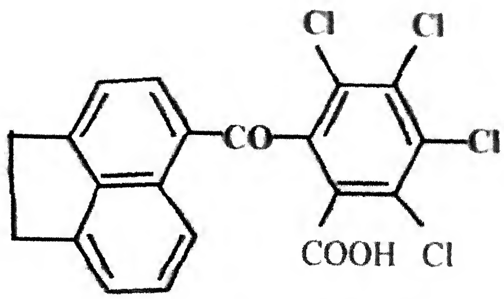
It was recrystallised from acetone, it gives positive tests for carboxyl and chlorine groups and was identified and confirmed as 2-(5'-chloro-2'-chloromethyl benzoyl) tetrachloro benzoic acid by mixed melting point determination and superimposition of IR spectra with that of the original sample.

Identification of residue III :

The purified residue melted at 109-110 ^{0} C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observation, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in chart E chapter II.

DYES DERIVED FROM 2-(3'- ACENAPHTHOYL)-TETRACHLORO BENZOIC ACID)



B.4 PREAPARATION OF 2-(3' ACENAPHTHOYL) TETRA CHLORO BENZOIC ACID.

The acid was prepared by carrying out Fridedl- Crafts reaction between acenaphthene and tetra chlorophthalic anhydride in presence of anhydrous aluminium chloride as catalyst. Nitro benzene has been used as the solvent. Starting from acenaphthene (15.5g, 0.1mole); tetrachloro phthalic anhydride, (28.6g, 0.1mole) anhydrous aluminium chloride (27.0g 0.2mole) and 100ml of nitro benzene, the yield of the acid obtained was 20.7g (47%). The crude acid was crystallised first from hot water and then recrytstallised from aqueous ethanol in the form of yellowish white crystalline solid, m.p. 260-262^0 C (decomp.). The acid is soluble in ethanol and hot water.

Anal. For : $C_{20}H_{10}O_3Cl_4$ (Mol. Wt. 440)

Calc : C, 54.54; H, 2.27; Cl, 32.27;

Found : C, 54.38; H, 2.26 Cl, 32.14;

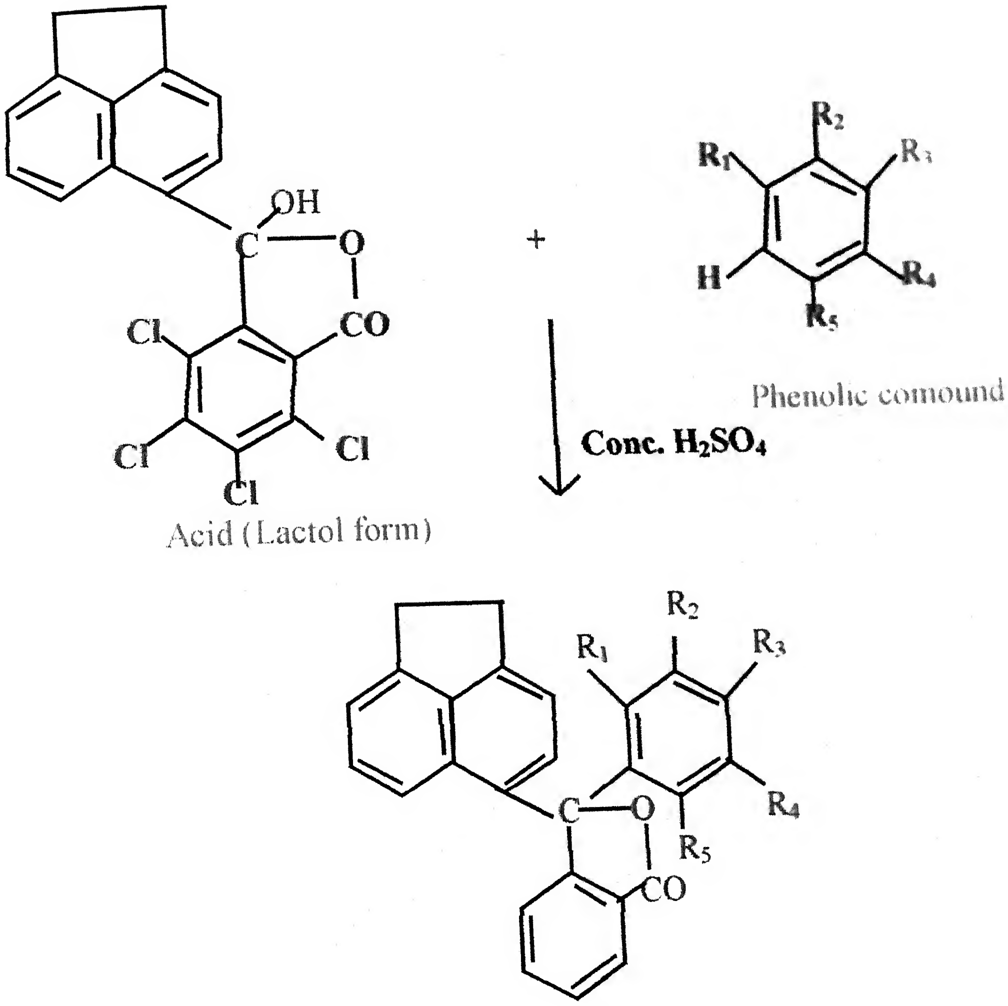
B. 4.1 PREPARATION OF ACETYL DERIVATIVE OF 2-(3' ACENAPHTHOYL) TETRA CHLORO BENZOIC ACID :

The acid (1.0g) was acetylated isolated and purified as A 4.1 chapter III. The brown coloured acetylated acid (0.73g) having m.p. 160-162^0 C; is soluble in chloroform, acetone , ethanol and in acetic acid.

Anal. For : $C_{20}H_9O_3Cl_4(OCCH_3)$ (Mol. Wt. 482)

Calc : C, 49.79; H, 1.86; Cl, 29.46; acetyl, 8.92;

Found : C, 49.62; H, 1.80; Cl, 29.32; **acetyl, 8.86;**



Dye molecule

B. 4.2 3 - **Acenaphthyl phenol tetrachloro pathal-as-ein.**
$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

B. 4.3 3 – **Acenaphthyl resorcinol tetrachloro pathal-as-ein.**
$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

B. 4.4 3 – **Acenaphthyl catechol tetrachloro pathal-as-ein.**
$R_3 = R_4 = R_5 = H$; $R_1 = R_2 = OH$

B. 4.5 3 – Acenaphthyl hydroquinone tetrachloro pathal-as-ein.
$R_2 = R_3 = R_5 =$ H; $R_1 = R_4 =$ OH

B. 4.6 3 – Acenaphthyl pyrogallol tetrachloro pathal-as-ein.
$R_4 = R_5 =$ H; $R_1 = R_2 = R_3 =$ OH

B. 4.7 3 – Acenaphthyl phloroglucinol tetrachloro pathal-as-ein.
$R_2 = R_4 =$ H; $R_1 = R_3 = R_5 =$ OH

B. 4.8 3 – Acenaphthyl diacetyl resorcinol tetracholo pathal-as-ein.
$R_2 = R_4 = R_5 =$ H; $R_1 = R_3 = OCOCH_3$

B. 4.9 3 – Acenaphthyl dibromo resorcinol tetracholo pathal-as-ein.
$R_5 =$ H; $R_1 = R_3 =$ H; $R_2 = R_4 =$ Br.

B.4.2 PREAPARATION OF (3-ACENAPHTHYL PHENOL TETRACHLORO PHTAHL-AS-EIN:

It was prepared, isolated and purified exactly in the same manner as mentioned in the case of A.4.2 chapter III, yield 50%.

The crystalline brown dye has m.p. 249-251^0 C . It dissolves in ethanol giving light brown colour, which turns into pink on addition of a drop of alkali. In strong basic medium it gives pink colour.

Anal. For : $C_{26}H_{14}O_3Cl_4$ (Mol. Wt. 516)

Calc : C, 60.46; H, 2.71; Cl, 27.51;

Found : C, 60.25; H, 2.67 Cl, 27.42;

B. 4.3 PREPARATION OF 3- ACENAPHTHYL RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared, isolated and purified as A. 4.3 chapter III, yield 60%.

The reddish brown crystalline dye having m.p.291-293^0 C, is soluble in ethanol, acetone, ether and acetic acid. It dissolve in ethanol giving yellow colour, which turns into yellowish green fluorescence in moderate as well as in strong basic mediums.

Anal. For : $C_{26}H_{14}O_4Cl_4$ (Mol. Wt. 532)

Calc : C, 58.66; H, 2.63; Cl, 26.69;

Found : C, 58.48; H, 2.56 Cl, 26.52;

B.4.4 PREPARATION OF 3-ACENAPHTHYL CATECHOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared isolated and purified similarly as described in the case of A.4.3 chapter III, yield 45%.

The black amorphons dye, m.p. 260^0 C (decomp-), dissolves in ethanol giving blackish green colour in moderate as well as strong medium it shows blackish green colour.

Anal. For : $C_{26}H_{14}O_4Cl_4$ (Mol. Wt. 532)

Calc : C, 58.66; H, 2.63; Cl, 26.69;

Found : C, 58.52; H, 2.61 Cl, 26.53;

B.4.5 PREPARATION OF 3-ACENAPHTHYL HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared, isolated and purified as A.4.3 chapter III, yield 50%.

The reddish black, amorphous dye has m.p. 144-146^0 C. It dissolves in ethanol giving red colour. It gives deep red colour both in moratede and strong basic mediums.

Anal. For : $C_{26}H_{14}O_4Cl_4$ (Mol. Wt. 532)

Calc : C, 58.66; H, 2.63; Cl, 26.69;

Found : C, 58.48; H, 2.57 Cl, 26.63;

B.4.6 PREPARATION OF 3-ACENAPHTHYL PYROGALLOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared, isolated and purified in the same manner as described in the case of A.4.3 chapter III, yield 54%.

The crystalline dark brown, dye has m.p. > 300^0 C. Its ethanolic solution gives brown colour, which turns violet on adding a drop of alkali. With 2% caustic soda solution it shows violet colour.

Anal. For : $C_{26}H_{14}O_5Cl_4$ (Mol. Wt. 548)

Calc : C, 56.93; H, 2.55; Cl, 25.91;

Found : C, 56.79; H, 2.50 Cl, 25.80;

B.4.7 PREPARATION OF 3-ACENAPHTHYL PHLOROGLUCINOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared isolated purified exactly in the same manner as mentioned in the case of A.4.3 chapter III.

The dark brown, crystalline dye has, m.p. >300^0 C. Its ethanolic solution is light brown coloured which becomes intense on adding a drop of alkali. In strong basic medium it shows deep brown colour.

Anal. For : $C_{26}H_{14}O_5Cl_4$ (Mol. Wt. 548)

Calc : C, 56.93; H, 2.55; Cl, 25.91;

Found : C, 56.74; H, 2.49 Cl, 25.78;

B.4.8 ACETYHLATION OF 3-ACENAPHTHYL RESORCINOL TETRACHLORO PHTHAL-AS EIN

(3-Acenaphthyl diacetyl resorcinol tetrachloro phthal-as-ein)

The dye, 3-acenaphthyl resorcinol tetrachloro phthal-as-ein (1.0g) was acetylated, isolated exactyl in the same way as A.4.8 chapter III.

The crude dark yellow coloured product was decolourised by treating with animal charcoal and was finally crystallised from acetone, yield 65%.

The light yellow coloured acetyl derivative, m.p. 245-247^0 C, dissolves in ethanol giving coloured solution. In alkaline medium it shows pinkish green fluorescence.

Anal. For : $C_{26}H_{12}O_4Cl_4(COCH_3)_2$. (Mol. Wt. 616)

Calc : C, 50.66; H, 1.94; Cl, 23.05; Acetyl, 13.96.

Found : C, 50.48; H, 1.90; Cl, 22.96; Acetyl, 13.90.

B.4.9 BROMINATION OF 3-ACENAPHTHYL RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

(3- Acenaphthyl dibromo resorcinol tetrachloro phthal-as-ein)

Starting with 1.0g of the dye, the preparation isolation and purification of its dibromo derivative, were carried out in a similar manner as described in the case of A.4.9 chapter III.

The black red crystalline dye, m.p. 165^0 C (decomp.), is soluble in ethanol and acetic acid. It dissolves in ethanol giving yellowish orange colour, which shows reddish orange green fluorescence, on adding a drop of alkali. With 2% caustic soda solution it gives deep red colour.

Anal. For : $C_{26}H_{12}Cl_4Br_2O_4$ (Mol. Wt. 690)

Calc : Br, 23.18;

Found : Br, 23.06;

B.4.10 CAUSTIC POTASH TREATMENT OF 3-ACENAPHTHYL RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

The dye (1.0g) was subjected to caustic potash fusion as in case of A.4.10 chapter III as a result the following three residues were collected.

Examination of red coloured residue (I) :

It was identified as the unreacted residual dye from its colour reactions and mixed melting point determination with the authentic sample of the dye.

Examination of yellowish white residue (II) :

It was purified by crystallization from aqueous ethanol. It gave positive test for carboxyl group and was confirmed to be 2-(3'- acenaphthoyl) tetrachloro benzoic acid from mixed melting point determination. There was no depression in meting point when mixed with the authentic sample of the acid.

Examination of brownish red residue (III) :

It was identified as resorcinol as in case of A.4.10 chapter III.

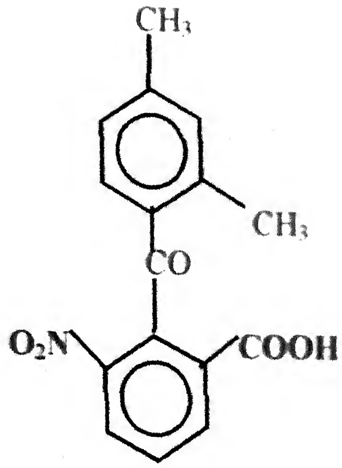
Acetylation, bromination and caustic potash fusion of the resorcinol dye are shown in chart G chapter II.

CHAPTER

FIVE

EXPERIMENTAL-C

DYES DERIVED FROM 2-(2' 4' DIMETHYL BENZOYL) 3-NITRO BENZOIC ACID:



2-(2' 4' dimethyl benzoyl)-3- nitrobenzoic acid

C.1 PREPARATION OF 2-(2' 4' DIMETHYL BENZOYL) NITRO BENZOIC ACID:

The acid was prepared by carrying out Friedel Crafts reaction between m-xylene (dry AR 100ml.) and 3-nitro phthalic anhydride (20.0g, 0.1mole) with anhydrous aluminium chloride (27.0g, 0.2mole) used as a catalyst. The reaction was carried out in one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap aluminium chloride in installment. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until the evaporation of hydrogen chloride ceased.

The heavy dark coloured complex was decomposed by adding 30ml of concentrated hydrochloricacid (in250ml ice cold water). The excess of m-xylene was removed by distillation. The residue was extracted three four times with boiling 10% solution of Na_2CO_3 and filtered. The acid was precipitated from the filtrate by the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and crystallized from acetone. The white crystalline acid m.p. 127-129^0 C, yield 21.0g. It is soluble in ether, acetone and methanol.

Anal. For : $C_{16}H_{13}NO_5$ (mol. wt. = 299)

Calc. : C, 64.21; H. 4.35; N, 4.68;

Found : C, 64.02; H,4.29; N, 4.63;

C.1.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

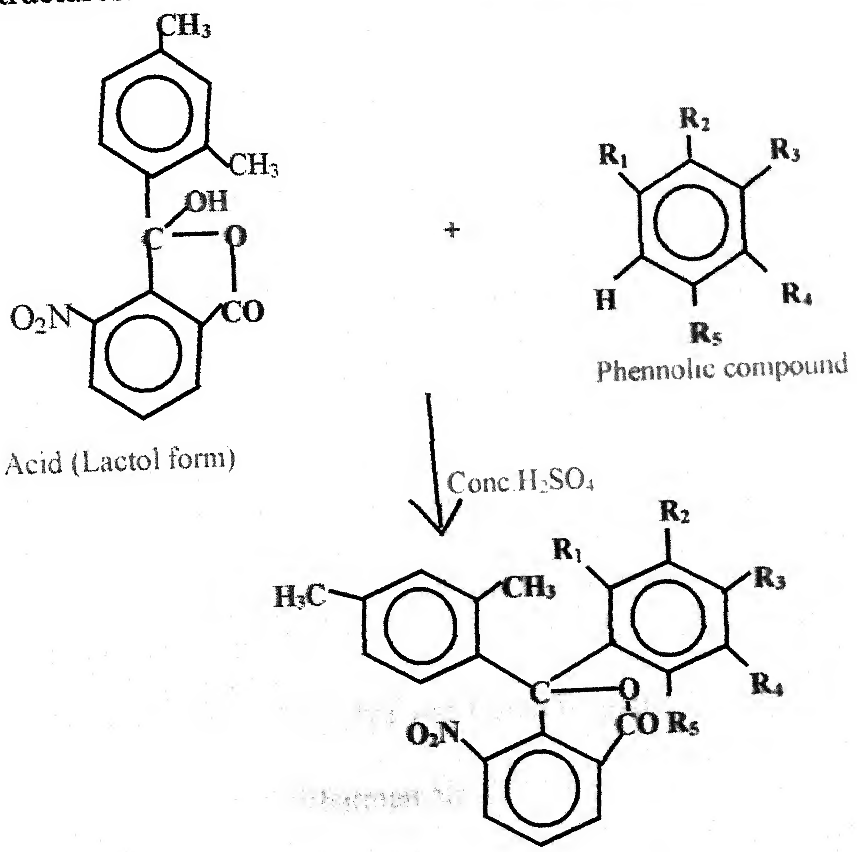
The acid (1.0g) and fused sodium acetate (3.0g) were refluxed with 20ml of freshly distilled acetic anhydride at 125-135^0 C for four hours. The hot contents were poured into a beaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of brown coloured solid mass. The coloured acid derivative was decolourized by treatment with animal charcoal. It was crystallized from acetone in the form of amorphous solid, m.p. 117-118^0 C. It is soluble in acetone, chloroform and acetic acid, yield 0.75g.

Anal. : $C_{18}N_{15}NO_6$ or $C_{16}H_{12}NO_5$ $(OC.CH_3)$ (mol. wt. = 341)

Calc. : C, 63.34; H, 4.37;N, 4.41; acetyl. 12.61;

Found : C, 63.18; H, 4.37; N, 4.10; acetyl. 12.56;

The dyes prepared from the acid may be represented by the following structures.



Dye molecule

C.1.2 (2, 4 dimethyl phenyl) phenol nitro phthal-as-ein
$R_1 = R_2 = R_4 = R_5 = H$, $R_3 = OH$;

C.1.3 (2, 4 dimethyl phenyl) resorcinol nitro phthal-as-ein
$R_2 = R_4 = R_5 = H$, $R_1 = R_3 = OH$;

C.1.4 (2, 4 dimethyl phenyl) catechol nitro phthal-as-ein
$R_3 = R_4 = R_5 = H$, $R_1 = R_2 = OH$;

C.1.5 (2, 4 dimethyl phenyl) hydroquinone nitro phthal-as-ein
$R_2 = R_3 = R_5 = H$, $R_1 = R_4 = OH$;

C.1.6 (2, 4 dimethyl phenyl) pyrogallol nitro phthal-as-ein
$R_4 = R_5 = H$, $R_1 = R_2 = R_3 = OH$;

C.1.7 (2, 4 dimethyl phenyl) phloroglucinol nitro phthal-as-ein
$R_2 = R_4 = H$, $R_1 = R_3 = R_5 = OH$;

C.1.8 (2, 4 dimethyl phenyl) diacetyl resorcinol nitro phthal-as-ein
$R_2 = R_4 = R_5 = H$, $R_1 = R_3 = OCOCH_3$

C.1.9 (2, 4 dimethyl phenyl) dibromo resorcinol nitro phthal-as-ein
$R_5 = H$, $R_1 = R_3 = OH$, $R_2 = R_4 = Br$

C.1.2 PREPARATION OF (2, 4 DIMETHYL PHENYL)-PHENOL NITRO PHTHAL-AS-EIN :

The acid (1.5g) and phenol (1.0g) were condensed in an oil bath in presence of 4-5 drops of concentrated sulphuric acid at 160-170^{0}C for about four and half hours till the molten mass of the flask became brittle on cooling. The condensed mass was taken out from the flask and subjected to steam distillation to remove excess of phenol. The buff coloured tube solid mass left in the flask was powdered and extracted with 2% NaOH solution. It was filtered and the dye was precipitated from filtrate by the gradual addition of hydrochloric acid with constant stirring. It was purified by repeated crystallization from rectified spirit and dried in a vacuum desiccator, yield 1.2g.

The purity of the dye was tested by paper chromatography.

Paper Whatman No 1

Mobile phase	Butanol saturated with ammonia
Developing agent	1% aqueous caustic soda
Reference dye	Phenolphthlein

A 25- x 10-cm strip was taken and a very dilute solution of the dye was spotted on the paper on a base line 4.0 cm from the end) with a micro syringe. Similarly, a dilute aqueous solution of the reference dye was also spotted on the base line about 3.0 cm from the first spot. The mobile phase was allowed to run for thirteen hours. The paper was then taken out, dried and sprayed. Chromatogram of each dye gave only one corresponding spot. This confirmed the homogeneity and purity of the dye.

Found : R_1 (phenolphthathalein): 0.93

: Rf [(2, 4 dimethyl phenyl) phenol phthal-as-ein] : 0.95

Reported : Rf (phenolphthalein): 0.92

The brown coloured micro-crystalline dye m.p. 117-118^{0}C gives light yellow colour in ethanol which turns into light violet on adding a drop of an alkali. It is soluble in benzene, acetone and ethanol.

Anal. For	: $C_{22} H_{17} NO_5$ (mol. wt. 375)
Calc.	: C, 70.40; H, 4.53; N, 3.73;
Found	: C, 70.19; H, 4.50; N, 3.68;

C.1.3 PREPARATION OF (2, 4 DIMETHYL PHENYL)-RESORCINOL NITRO PHTHAL-AS-EIN:

It was prepared by condensing an intimate mixture of the acid (3.0g) and resorcinol (3.0g) in the oil bath in presence of 4-5 drops of concentrated sulphuric acid at 150-160^{0}C for about four and half hours till the molten mass became hard and brittle on cooling. The condensed mass was crushed and washed with an excess of water to remove excess of resorcinol. It was extracted with 2% aqueous solution of caustic soda and filtered. The dye was precipitated from reddish brown with green fluorescent filtrate by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 80^{0}C and then in a vacuum desiccator, yield 3.5g.

The brown microcrystalline dye having m.p. 284-286°C, is soluble in benzene, ethanol, methanol and acetic acid. Its ethanolic solution is brown which alters to brownish red with green fluorescence on adding a drop of an alkali. In strong basic medium, reddish brown colour is obtained.

Anal. For : $C_{22}H_{17}NO_6$ (Mol. Wt. 391)

Calc. : C, 67.52; H, 4.35; N, 3.58;

Found : C, 67.44; H, 4.32; N, 3.56;

C.1.4 PREPARATION OF (2,4-DIMETHYL-PHENYL)-CATECHOL-PHTHAL-AS-EIN :

The dye was prepared by heating a homogeneous mixture of the acid (1.2g) and catechol (1.5g) in an oil bath at 120-130°C in presence of 4-5 drops of concentrated sulphuric acid for about four hours. The isolation and purification of the dye were done as in the case of (2, 4 dimethyl phenyl) resorcinol nitro phthal-as-ein. Yield 1.5g.

The dye is black in colour, m.p. above 360°C. Its ethanolic solution is brown in colour. It gives blackish brown colour on addition of alkali. It is soluble in acetone, ethanol and acetic acid.

Anal. For : $C_{22}H_{17}NO_6$ (Mol. Wt. 391)

Calc. : C, 67.52; H, 4.35; N, 3.58;

Found : C, 67.38; H, 4.32; N, 3.55;

C.1.5 PRERATION OF (2,4 DIMETHYL PHENYL) HYDROQUINONE NITRO PHTHAL-AS-EIN:

It was prepared by condensing a homogeneous mixture of the acid (1.5g) and hydroquinone (1.2g). The intimate mixture was heated on oil bath at 160-170°C in presence of 4-5 drops of concentrated sulphuric acid for about four hours till the molten mass became hard and brittle on cooling. The isolation and purification of the dye were done as in the case of (2, 4 dimethyl phenyl) resorcinol nitro phthal-as-ein, yield 1.5g.

The black coloured dye having m.p. 210°C, is soluble in chloroform, ethanol and methanol. Its alcoholic solution gives light brown colour that turns into dark brown on addition of an alkali.

Anal. For : $C_{22}H_{17}NO_6$ (Mol. Wt. 391)

Calc. : C, 67.52; H, 4.35; N, 3.58;

Found : C, 67.41; H, 4.30; N, 3.56;

C.1.6 PREPARATION OF (2-4 DIMETHYL PHENYL) PYROGALLOL NITRO PHTHAL-AS-EIN :

The mixture of acid (1.0g) and pyrogallol (1.0g) was heated in the oil bath in the presence of 4-5 drops of concentrated sulphuric acid at 130-150 ^{0}C for about four hours. The dye was isolated and purified in a manner similar to the other dyes, yield 1.0g.

The black shining crystals having a m.p. above 360^{0}C, is soluble in ethanol, methanol and acetic acid. It dissolves in ethanol yielding light brown colour which turns violet on addition of a drop of an alkali.

Anal. For : $C_{22}H_{17}NO_7$ (Mol. Wt. 407)

Calc. : C, 64.86; H, 4.18; N, 3.44;

Found : C, 64.75; H, 4.16; N, 3.39;

C.1.7 PREPARATION OF (2,4 DIMETHYL PHENYL) PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

It was prepared by condensing a homogenous mixture of the acid (1.0g) and phloroglucinol (1.2g). The intimate mixture was heated on oil bath at 190-200^{0}C for about four hours. The dye was isolated and purified in a manner similar to C.1.3 dye chapter V, yield 1.29.

The brownish red dye decomposed at 340^{0}C gives brown colour with ethanol, which turns into red on adding a drop of an alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal. For : $C_{22}H_{17}NO_7$ (Mol. Wt. 407)

Calc. : C, 64.86; H, 4.18; N, 3.44;

Found : C, 64.68; H, 4.16; N, 3.42;

C.1.8 PREPARTION OF (2,4 DIMETHYL PHENYL) DIACETYL RESORCINOL NITRO PHTHAL-AS-EIN:

[Acetylation of (2,4 dimethyl phenyl) resorcinol phthal-as-ein]

The dye (2,4 dimethyl phenyl) resorcinol nitro phthal-as-ein (1.0g) and fused sodium acetate (3.0g) with 15.0ml of freshly distilled acetic anhydride were taken in a sodium acetate (3.0g) with 15.0 ml of freshly distilled acetic anhydride were taken in a 50 ml round bottomed flask fitted with an air condenser. The contents refluxed at 130-140^{0}C for about four hours. The hot contents were poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon the light yellow solid settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallized from aqueous ethanol and a little acetic acid. It was dried in an oven at 40^{0}C and then over phosphorus pentoxide under reduced pressure, yield 0.70g.

The crystalline acetyl derivative is yellow coloured and has a m.p. of 235-236^{0}C.

It is soluble in benzene, ether, chloroform and acetic acid.

Anal. For	: $C_{26}H_{21}NO_8$ or $C_{22}H_{15}NO_6\,(COCH_3)_2$ (Mol. Wt. 475)
Calc.	: C, 65.68; H, 4.42; Acetyl 18.11;N, 2.95;
Found	: C, 65.50; H, 4.40; Acetyl 18.07;N, 2.90;

C.1.9 BROMINATION OF (2,4 DIMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

[(2,4 DIMETHYL PHENYL) DIBROMO RESORCINOL PHTHAL-AS-EIN]

The dye (2,4 dimethyl phenyl)- resorcinol-phthal-as-ein (1.0g) was dissolved in minimum quantity of glacial acetic acid and 15ml of a 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with air condenser and the contents were refluxed at 120-130 ^{0}C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dirty orange powder settled down. It was filtered and washed well with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude brominated dye was finally purified by crystallization from aqueous ethanol and dried at 80^{0}C in an oven and then in a vacuum desiccator, yield 1.0g.

The dirty orange crystalline compound decomposed at 212°C, is soluble in benzene, ether, chloroform, acetone, and acetic acid.

Anal. For : $C_{22}H_{15}NO_6Br_2$ (Mol. Wt. 549)

Calc. : Br, 29.14

Found : Br, 29.05

C.1.1. CAUSTIC POTASH TREATMENT OF (2,4 DIMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

Potassium hydroxide pellets (10.0g) were taken in a crucible and heated with a few drops of water to make a paste. The dye (1.0g) was then added to it. The contents were heated for about four hours till the darkened colour of the dye faded completely. After cooling, the contents were diluted with 50 ml of the water and filtered. The dark residue (I) settled down on just neutralizing the alkali. It was filtered and washed well with water. The filtrate, when acidified further by adding excess of dilute hydrochloric acid gave white precipitate (II), which was filtered and washed with water. It was crystallized from aqueous ethanol and dried in a vacuum desiccator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Residue-I

It was identified and confirmed to be the unreacted dye from its colour reactions and determination of the mixed melting point with the authentic sample.

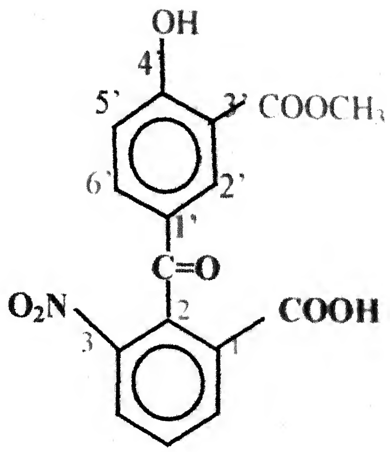
Residue II

It was acidic in nature and gave positive tests for the presence of carboxylic groups. It was identified as 2-(2,4 dimethyl benzoyl) benzoic acid and confirmed by mixed melting point determination (m.p. 127-129°C) and by superimposition of the IR spectra of the authentic sample.

Residue III

The purified sample melted at 109-110°C. It gave positive tests with ferric chloride, Fehling's solution and ammoniacal silver nitrate. It gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol. Acetylation, bromination and caustic potash treatment of the dye are shown in chart A in chapter II.

DYES DERIVED FROM 2-(3'-CARBMETHOXY 4'-HYDROXY BENZOYL) 3-NITRO BENZOIC ACID :



C.2 PREPARATION OF 2-(3'-CARBMETHOXY-4'-HYDROXY BENZOYL)-3- NITRO BENZOIC ACID:

The acid was prepared isolated by carrying out Friedel Crafts reaction between methyl salicylate (dry AR 80ml), and 3 nitro phthalic anhydride (20.0g, 0.1mole) in presence of anhydrous aluminium chloride (27.0g, 0.2mole) as the acid C.1 chapter V. The acid was crystallised from hot water in the form of white crystalline solid, m.p. 253-54°c acetone, yield 15.0g.

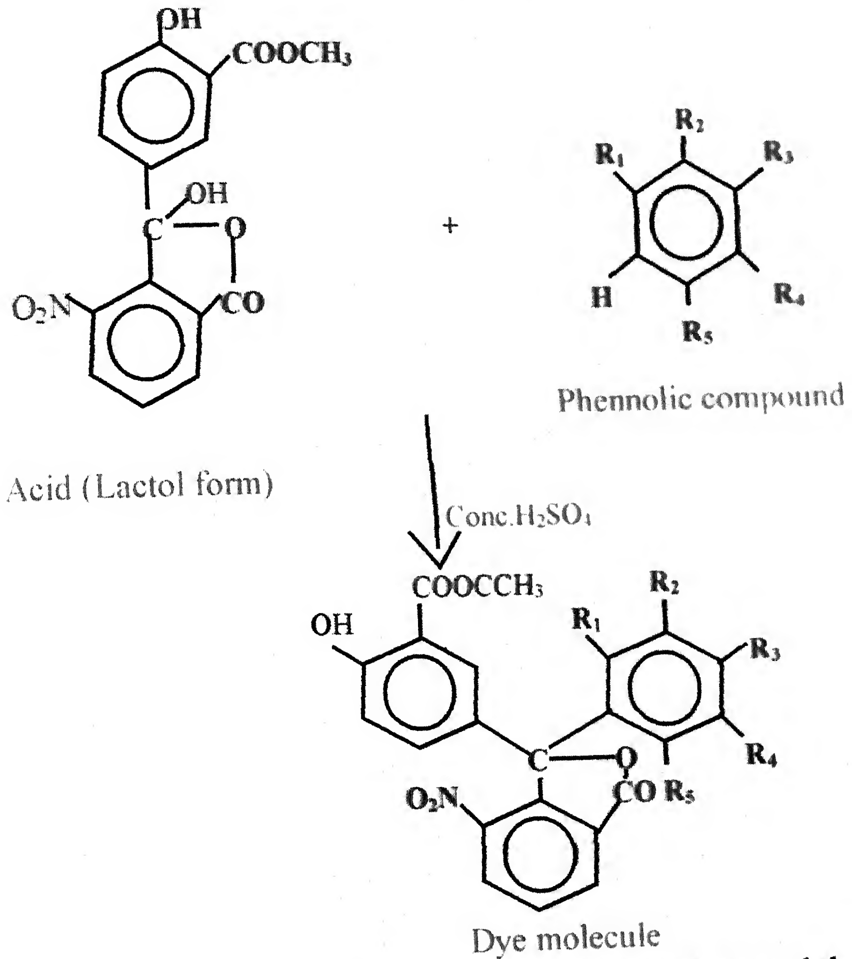
Anal. For.	: $C_{16}H_{11}NO_8$ (mol. wt. = 345)
Calc.	; C, 55.65; H, 3.19; N, 4.06;
Found	: C, 55.47; H, 3.16; N, 4.04;

C.2.1 PREPARATION OF ACETYL DERVATIVE OF THE ACID :

The acetyl derivative of the acid was prepared and isolated by taking (1.0g) acid, (3.5g) of fused sodium acetate and 15ml of acetic anhydride in similar manner as acetyl derivative C.1.1 chapter V. The coloured acetyl derivated was treated with animal charcoal till decolourised and finally recrystallised from acetone. The yield 0.9g m.p. 115^0 C (Decomposed). It is soluble in acetone, chloroform and acetic acid.

Anal. For.	: $C_{20}H_{15}NO_{10}$ or $C_{16}H_9NO_8\ (COCH_3)_2$ (mol.wt.429)
Calc.	: C, 55.94; H, 3.49; N,3.25; acetyl. 20.05;
Found	: C,55.78; H, 3.47; N, 3.25; acetyl. 20.00;

The dyes prepared from the acid may be represented by the following general formula :-



C.2.2 (3-carbmethoxy 4-hydroxy phenyl) phenol nitro phthal-as-ein.
$R_1 = R_2 = R_4 = R_5 = H; R_3 = OH$

C.2.3 (3-carbmethoxy 4-hydroxy phenyl) resorcinol nitro phthal-as-ein.
$R_2 = R_4 = R_5 = H; R_1 = R_3 = OH$

C.2.4 (3-carbmethoxy 4-hydroxy phenyl) resorcinol nitro phthal-as-ein.
$R_1 = R_2 = OH; R_3 = R_4 = R_5 = H$

C.2.5 (3-carbmethoxy 4-hydroxy phenyl) hydroquuinone nitro phthal-as-ein.
$R_2 = R_3 = R_5\ H; R_1 = R_4 = OH$

C.2.6 (3-carbmethoxy 4-hydroxy phenyl) pyrogallol nitro phthal-as-ein.
$R_1 = R_2 = R_3$ OH; $R_4 = R_5 = H$

C.2.7 (3-carbmethoxy 4-hydroxy phenyl) phloroglucinol nitro phthal-as-ein.
$R_1 = R_3 = R_5$ OH; $R_2 = R_4 = H$

C.2.8 (3-carbmethoxy 4-hydroxy phenyl) diacetyl resorcinol nitro phthal-as-ein.
$R_2 = R_4 = R_5$ H; $R_1 = R_3 = OCOCH_3$

C.2.9 (3-carbmethoxy 4-hydroxy phenyl) dibromo resorcinol nitro phthal-as-ein.
$R_5 = H$; $R_1 = R_3$ OH; $R_2 = R_4 = Br$

C.2.2 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) PHENOL PHTHAL-AS-EIN :

The dye was prepared by condensing the acid (1.5g) and phenol (1.2g) in presence of few (4-5) drops of concentrated sulphuric acid. The heating was carried out for four hours at 175-180^0 C, till brittle mass was obtained on cooling. Excess of phenol was removed by steam distillation. The mass left in the flask was powdered and extracted with 2% sodium hydroxide solution. It was filtered and the dye was precipitated from coloured filtrate by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallization from rectified spirit and dried in vacuum desiccator, yield 1.3g. The purity of the dye was tested by paper chromatography as in case of C.1.2 chapter V.

The orange coloured dye has m.p.135-136^0 C. Its ethanolic solution is brownish-red in colour, which turns into pink on adding a drop of alkali.

Anal. For.	: $C_{22}H_{15}NO_8$ (Mol.Wt. 421)
Calc.	: C, 62.71; H, 3.56; N, 3.33;
Found	: C, 62.52; H,3.54; N, 3.30;

C.2.3 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (2.5g) and resorcinol (2.5g) in presence of 6-7 drops of concentrated sulphuric acid. Heating was continued for four and half hours at 130-148^0 C, till brittle mass was obtained on cooling. The isolation and purification were done as in the case of C 1.3 chapter V, yield 4.5g.

The red microcrystalline dye having m.p. 190-192^0 C is soluble in benzene chloroform ethanol and methanol. Its ethanolic solution is yellowish red with green fluorescence and turns into yellowish orange with green fluorescence on adding a drop of alkali. In strong basic medium it gives reddish brown colour with green fluorescence.

Anal. For. : $C_{22}H_{15}NO_9$ (mol. wt. 437)

Calc. : C, 60.41; H, 3.43; N, 3.20;

Found : C, 60.28; H, 3.41; N, 3.18;

C.2.4 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) CATECHOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (1.5g) and catechol (1.0g) in presence of conc. Sulphuric acid (5-6 drops) at the temp. 140-150^0 C for four hours, till molten mass becomes hards brittle on cooling. The isolation and purification were done as in the case of C 1.3 chapter V, yield 1.0g.

The dye is black in colour, m.p. above 360^0 C. Its ethanolic solution is brown in colour which turns into brownish black on adding adrop of alkali.

Anal. For. : $C_{22}H_{15}O_9$ (mol. wt. 437)

Calc. : C, 60.41; H, 3.43; N, 3.20;

Found : C, 60.24; H, 3.40; N, 3.18;

C.2.5 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) HYDROQUINONE NITRO PHTHAL-AS-EIN :

The dye was prepared by heating the homogeneous mixture of the acid (1.5g) and hydroquinone (1.0g) in an bath at the temp. 160-180^0 C for about four hours in presence of 5-6 drops of concentrated sulphuric acid. The isolation and purification were done similarly as in the case of C.1.3 chapter V, yield 1.5g

The black coloured dye decomposes above 300^0 C. Its ethanolic solution is (light brown) in colour.It gives brown colour on addition of alkali. It is soluble in ethanol, methanol and acetic acid.

Anal. For. : $C_{22}H_{15}NO_9$ (mol. wt. 437)

Calc. : C, 60.41; H, 3.43; N, 3.20;

Found : C, 60.23; H, 3.41; N, 3.17;

C.2.6 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) PYROGALLOL NITRO PHTHAL-AS-EIN :

It was prepared by carrying out the condensation of homogeneous mixture of the acid (1.5g) and pyrogallol (1.0g) in an oil bath in presence of 5-6 drops of conc. Sulphuric acid at the temperature 140-150^0 C for about four hours. The isolation and purification were done as in case of C 1.3 chapter V, yield 1.0g.

The shining black crystal decompose above 340^0 C. It is soluble in ethanol, methanol and acetic acid. Its ethanolic solution is light red in colour, which turns into violet on adding a drop of alkali.

Anal. For. : $C_{22}H_{15}NO_{10}$ (mol. wt. 453)

Calc. : C, 58.28; H, 3.31; N, 3.09;

Found : C, 58.16; H, 3.30; N, 3.06;

C.2.7 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) PHLOROGLUCINOL NITRO PHTHAL-AS-EIN :

An intimate mixture of the acid (1.5g) and phloroglucinol (1.0g) was heated in an oil bath to make it homogeneous and then 6-7 drops of conc. Sulphuric acid were added and heating was continued for about four hours at 180-200^0 C. The isolation and purification of the dye were dine in a similar manner as described in the case of (3-carbmethoxy 4-hydroxy phenyl) resorcinol nitro phthal-as-ein yield 1.2g.

The yellowish orange coloured dye has m.p. above 360^0 C. Its ethanolic solution is golden yellow in colour, which turns into reddish orange on addition of a drop of alkali. It is soluble in ethanol, methanol, acetone and acetic acid.

Anal. For. : $C_{22}H_{15}NO_{10}$ (mol. wt. 453)

Calc. : C, 58.28; H, 3.31; N, 3.09;

Found : C, 58.12; H, 3.30; N, 3.06;

C.2.8 ACETYLATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN :

[(4-acetoxy 3-carbmethoxy phenyl) diacetyl resorcinol nitro phthal-as-ein]

The dye (3-carbmethoxy 4-hydroxy phenyl) resorcinol phthal-as-ein (1.0g) and fused sodium acetate (3.0g) and freshly distilled acetic anhydride (15ml), were taken in a 50ml round bottom flask fitted with an air condenser. The purification and crystallization were done in a similar manner as in case of C. 1.8 chpater V. The acetylated compound was dried in an oven at 80^0 C and then over phosphorous penta-oxide under reduced pressure, yield 0.7g.

The acetylated product light yellow in colour m.p. $210\text{-}212^0$ C, is soluble in ether, methanol, chloroform and acetic acid.

Anal. For. : $C_{28}H_{21}NO_{12}$ $C_{22}H_{12}NO_9(OC\,CH_3)_3$ (mol. wt. 563)

Calc. : C, 59.68; H, 3.73; acetyl, 22.91;

Found : C, 59.46; H, 3.71; acetyl, 22.86;

C.2.9 BROMINATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN :

[(3-bromo 5-carbmethoxy 4-hydroxy phenyl) dibromo resorcinol nitro phthal-as-ein]

The dye (3-carbmethoxy 4-hydroxy phenyl) resorcinol nitro phthal-as-ein (1.0g) was brominated, isolated and purified in a similar manner as in case of C. 1.9 chapter V yield 0.8g.

The pale-orange coloured dye has m.p. $248\text{-}250^0$ C. Its ethanolic solution is yellowish orange in colour. In moderate and strong basic medium it gives orange colour with green fluorescence.

Anal. For. : $C_{22}H_{12}Br_3NO_9$ (mol. wt. 674)

Calc. : Br, 35.61;

Found : Br, 35.48;

C.2.10 CAUSTIC POTASH TREATMENT OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN :

Caustic potash treatment of the resorcinol dye (1.0g) was carried out in identical manner as in the case of C.1.10 chapter V. As a result of fusion three residues were obtained.

Identification of residue – I

It was identified and confirmed as the unreacted residual dye from its colour reactions and mixed melting point determination with the authentic sample of the dye.

Identification of residue – II

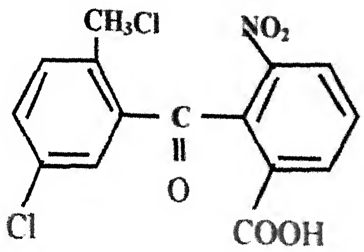
It was recrystallised from acetone, m.p.[illegible]°c It was acidic in nature and gave positive tests for carboxyl and phenolic groups. It was identified to 2-(3'-carbmethoxy 4'-hydroxy benzoyl) 3 nitro benzoic acid and confirmed by mixed melting point determination and superimposition of the IR spectra with the authentic sample.

Identification of residue – III

The purified sample melted at 109-110^0 C. It gave positive test with Fehling's solution, ferric chloride, ammonical silver nitrate. It gave fluorescein test with phthalic anhydride, on the basis of these observations it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are shown in chart C chapter II.

DYES DERIVED FROM 2-(5'-CHLORO-2'-CHLOROMEHYL BENZOYL) 3-NITRO BENZOIC ACID:



2-(5'-chloro-2'-chloromethyl benzoyl)-3- nitrobenzoic acid

C.3 PREPARATION OF 2-(5'-CHLORO-2'-CHLOROMETHYL BENZOYL) NITRO BENZOIC ACID:

The acid was prepared by carrying out Friedel Crafts reaction between para chlorobenzyl chloride and m-nitro phthalic anhydride and anhydrous $AlCl_3$. Starting with para chlorobenzylchloride (AR, dry 100ml), along with m-nitro phthalic anhydride (20.0g, 0.1mole) and anhydrous aluminum chloride (27.0g, about 0.2 moles) used as a catalyst, the acid was prepared following the procedure outlined in C .1 chapter V.

The acid was isolated as shining white crystals, which had melting point of 196-198^0 C. The crystalline solid was found to be soluble in rectified spirit and methanol, yield 15.0g.

Anal. For	: $C_{15}H_9NCl_2O_5$ (mol. wt. = 354)
Calc.	: C, 51.52; H. 2.78; N, 3.54; Cl, 17.93; acetyl. 10.86;
Found	: C, 51.40; H, 2.76; N, 3.52; Cl, 17.90; acetyl. 10.80;

C.3.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0g of acid 3.0g of fused sodium acetate was refluxed with 15ml of freshly distilled acetic anhydride at 130-140^0 C in the same way as in case of 2-(5'-chloro-2'-chloromethyl benzoyl) benzoic acid chapter III. It was crystallised

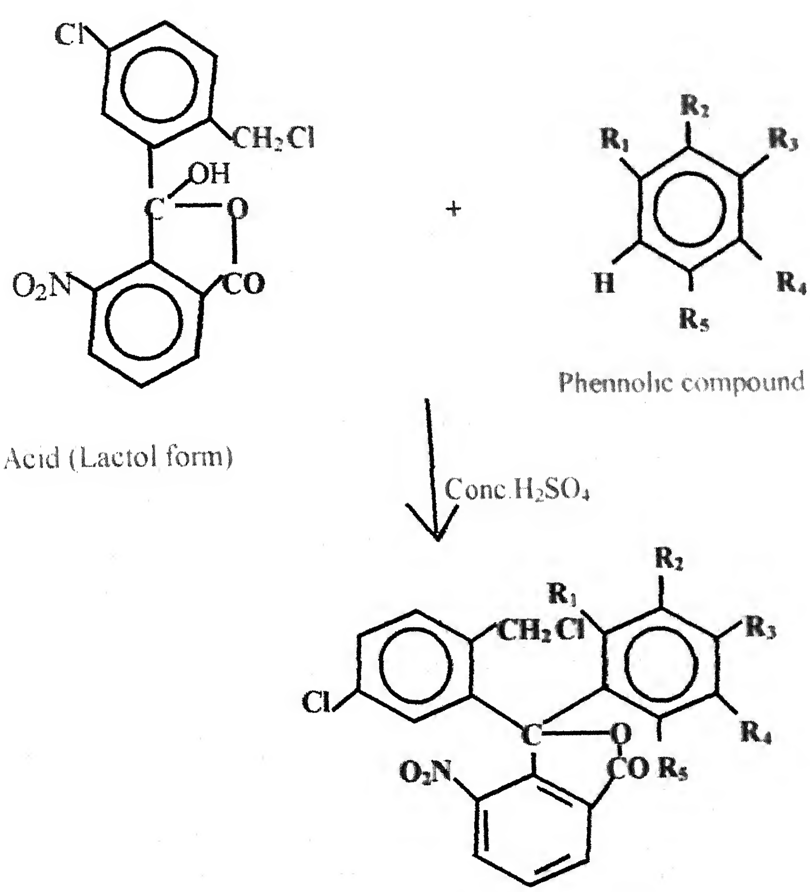
from acetone in the form of a black crystalline solid, m.p. 240^0 C. It is slightly soluble in methanol but highly soluble in acetone. Yield 0.60g.

Anal. : $C_{17}H_{11}NCl_2O_6$ or $C_{15}H_8NCl_2O_5(OC.CH_3)$ (mol. wt. = 396)

Calc. : C, 51.52; H, 2.78; N, 3.54; Cl, !7.93; acetyl. 10.86;

Found : C, 51.50; H, 2.76; N, 3.52; Cl, 17.90; acetyl. 10.80;

The dyes prepared from the acid may be represented by the following.



Dye molecule

DYES :

C.3.2 (5-chloro-2-chloromethyl phenyl) phenol nitro phthal-as-ein:
$R_1 = R_2 = R_4 = R_5 = H, R_3 = OH$

C.3.3 (5-chloro-2-chloromethyl phenyl) resorcinol nitro phthal-as-ein:
$R_2 = R_4 = R_5 = H, R_1 = R_3 = OH$

C.3.4 (5-chloro-2-chloromethyl phenyl) catechol nitro phthal-as-ein:
$R_3 = R_4 = R_5 = H$, $R_1 = R_2 = OH$

C.3.5 (5-chloro-2-chloromethyl phenyl) hydroquinone nitro phthal-as-ein:
$R_2 = R_3 = R_5 = H$, $R_1 = R_4 = OH$

C.3.6 (5-chloro-2-chloromethyl phenyl) pyrogallol nitro phthal-as-ein:
$R_4 = R_5 = H$, $R_1 = R_2 = R_3 = OH$

C.3.7 (5-chloro-2-chloromethyl phenyl) phloroglucinol nitro phthal-as-ein:
$R_2 = R_4 = H$, $R_1 = R_3 = R_5 = OH$

C.3.8 (5-chloro-2-chloromethyl phenyl) diacetyl resorcinol nitro phthal-as-ein:
$R_2 = R_4 = R_5 = H$, $R_1 = R_3 = 0.CO.CH_3$

C.3.9 (5-chloro-2-chloromethyl phenyl) dibromo resorcinol nitro phthal-as-ein:
$R_5 = H$, $R_1 = R_3 = OH$, $R_2 = R_4 = Br$

C.3.2 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) PHENOL NITRO PHTHAL-AS-EIN :

An intimate mixture of 2.0g of the acid and 1.5g of phenol was heated in a hard boiling tube to make it homogeneous. It was then condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-175^0 C for about four and half hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallization from rectified spirit and dried in vacuum in a desiccator, yield 1.20g.

The light pink dye has a m.p. 222-224^0 C. The ethanolic solution of the dye is light brown in colour that turns into violet colour on adding a drop of an alkali.

The purity of the dye was tested as done in the case of other phenol dyes described in earlier pages.

Anal. For. : $C_{21}H_{13}NCl_2O_5$ (mol. wt. 430)

Calc. : C, 58.60; H, 3.02; N, 3.26; Cl, 16.51;

Found : C, 58.42; H, 3.01; N, 3.22; Cl, 16.45;

C.3.3 PREPARAION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN :

The dye was prepared by heating mixture of 3.0g of the acid and 2.5g resorcinol in an oil bath at 120-130^0 C to make it uniform and homogeneous. Then the intimate mixture was condensed for four and half hours in presence of a few drops of concentrated sulphuric acid. The isolation and the purification of the dye were done in a manner similar to that in the case of C 1.3 chapter V, yield 0.6g.

The golden yellowish crystalline dye having a m.p. 225-227^0 C is soluble in ethanol to yield a brown colour in ethanol that turns to reddih brown with alcoholic caustic soda solution.

Anal. For. : $C_{21}H_{13}NCl_2O_6$ (mol. wt. 446)

Calc. : C, 56.50; H, 2.91; N, 3.14; Cl, 15.92;

Found : C, 56.37; H, 2.90; N, 3.11; Cl, 15.80;

C.3.4 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) CATECHOL NITRO PHTHAL-AS-EIN :

It was prepared by the condensation of 1.0g of the acid and 1.0g of catechol little excess than the molecular proportion on an oil bath in presence of 5-6 drops of concentrated sulphuric acid at 115-125^0 C for about four and half-hours. It was isolated and purified as described for C 1.3 chapter V, yield 0.8g.

The black crystalline dye having a m.p. 315-317^0 C, it dissolves in ethanol giving a brown colour with an alkali and reddish brown colour with 2% soda solution.

Anal. For. : $C_{21}H_{13}NCl_2O_6$ (mol. wt. 446)

Calc. : C, 56.50; H, 2.91; N, 3.14; Cl, 15.92;

Found : C, 56.27; H, 2.90; N, 3.12; Cl, 15.79;

C.3.5 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) HYDROQUINONE NITRO PHTHAL-AS-EIN :

1.5g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath 160-180^0 C for three hours in presence of a few drop of concentrated sulphuric acid, The isolation and purification of the dye was carried out in a manner similar to the one adopted for C .1.3 chapter V, yield 1.0g.

The blackish brown dye, having m.p. above 320-321^0 C is soluble in ethanol giving a brown colour that turns into reddish brown on the addition of 2% caustic solution.

Anal. For.	: $C_{21}H_{13}NCl_2O_6$ (mol. wt. 446)
Calc.	: C, 56.50; H, 2.91; N, 3.14; Cl, 15.92;
Found	: C, 56.32; H, 2.89; N, 3.11; Cl, 15.84;

C.3.6 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) PYROGALLOL NITRO PHTHAL-AS-EIN :

The intimate and homogenized mixture of 1.5g of the acid and 1.0g of pyrogallol was condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 190-200^0 C for about three hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for C 1.3 chapter V yield 0.80g.

The black coloured dye having m.p. above 340-342^0 C gives an ethanolic solution reddish brown in colour which on adding a drop of an alkali darkens in shade.

Anal. For.	: $C_{21}H_{13}NCl_2O_7$ (mol. wt. 462)
Calc.	: C, 54.55; H, 2.81; N, 3.03; Cl, 15.37;
Found	: C, 54.42; H, 2.80; N, 3.00; Cl, 15.25;

C.3.7 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) PHLOROGLUCINOL NITRO PHTHAL-AS-EIN :

The intimate and thoroughly homogeneous mixture of 1.0g of the acid and 1.0g of phloroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 180-200^0 C for about three hours. The isolation and purification of the dye was performed in the same way as that described for C 1.3 chapter V, yield 0.65g.

The brown coloured dye m.p. 292-294^0 C yields a wine red coloured solution in ethanol that turns dark red on adding a drop of an alkali. It gives wine red colour with alcoholic potash solution.

Anal. For. : $C_{21}H_{13}NCl_2O_7$ (mol. wt. 462)

Calc. : C, 54.55; H, 2.81; N, 3.03; Cl, 15.37;

Found : C, 54.40; H, 2.78; N, 3.00; Cl, 15.28;

C.3.8 ACETYLATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN :

[(5-CHLORO-2-CHLOROMETHYL PHENYL) DIACETYL RESORCINOL NITRO PHTHAL-AS-EIN :

1.0g of the 5-chloro-2-chloromethyl phenyl resorcinol nitro phthal-as-ein dye, 3.0g of fused sodium acetate and 15ml of reshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser and refluxed for about three hours. The isolation and purification of acetylated product was carried out in exactly the same manner as in the case of C 1.8 chapter V, yield 0.7g.

The buff coloured diacetyl derivative (m.p. 272-274^0 C) is soluble in acetone, methanol and chloroform.

Anal. For. : $C_{25}H_{17}NCl_2O_8$ or $C_{21}H_{11}NCl_2O_6(OC.CH_3)_2$ (mol. wt. 530)

Calc. : C, 56.60; H, 3.21; N, 2.64; Cl, 13.40; acetyl, 16.23;

Found : C, 56.48; H, 3.18; N, 2.58; Cl, 13.32; acetyl, 16.16;

C.3.9 BROMINATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

[(5-CHLORO-2-CHLOROMETHYL PHENYL) DIBROMO RESORCINOL NITRO PHTHAL-AS-EIN]

The 1.0g of the dye (5-chloro-2-chloromethyl phenyl) resorcinol nitro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10 ml of 10% solution of bromine in glacial acid was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed

at 120-130^0 C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A blackish rose powder settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 110^0 C in an oven then in a vacuum desiccator, yield 0.90g.

The yellowish orange coloured crystalline dye having m.p. 178-180^0 C is soluble in ethanol yielding a yellowish red colour that turns into orange with green fluorescence on adding a drop of an alkali. In strong alkaline medium, it exhibits deep red colour.

Anal. For. : $C_{21}H_{11}NBr_2Cl_2O_6$ (mol. wt. 604)

Calc. : Br, 26.49;

Found : Br, 26.42;

C.3.10 CAUSTIC POTASH TREATMENT OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN :

10.0g of potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to carry out the caustic potash treatment exactly in the same way as described in C 1.10 chapter V.

Identification of residue I :

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of residue II :

It was recrystallised from acetone. It gives tests for carboxyl group and chloride groups and was identified and confirmed as 2-(5'-chloro-2'-chloromethyl benzoyl) 3-nitro benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the original sample.

Identification of residue III :

The purified residue melted at 109-110^0 C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescence test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in chart E chapter II.

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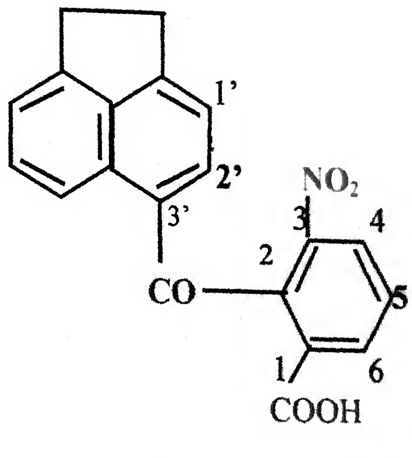
DYES DERIVEd FROM 2-(3'-ACENAPHTHOYL)-3- NITRO BENZOIC ACID



The acid was prepared by carrying out Friedel-Crafts reaction between acenaphthene and 3 nitro phthalic anhydride in presence of anhydrous aluminium chloride as catalyst and nitro benzene was used as solvent. The preparation and isolation of acid were carried out as in case of (C.1 chapter V). The acid was crystallized from aqueous ethanol in the form of white needles having m.p. 208-210^{0}C.The acid is soluble in ethanol, ether, chloroform, and sparingly soluble in benzene and insoluble in carbondisul phide.

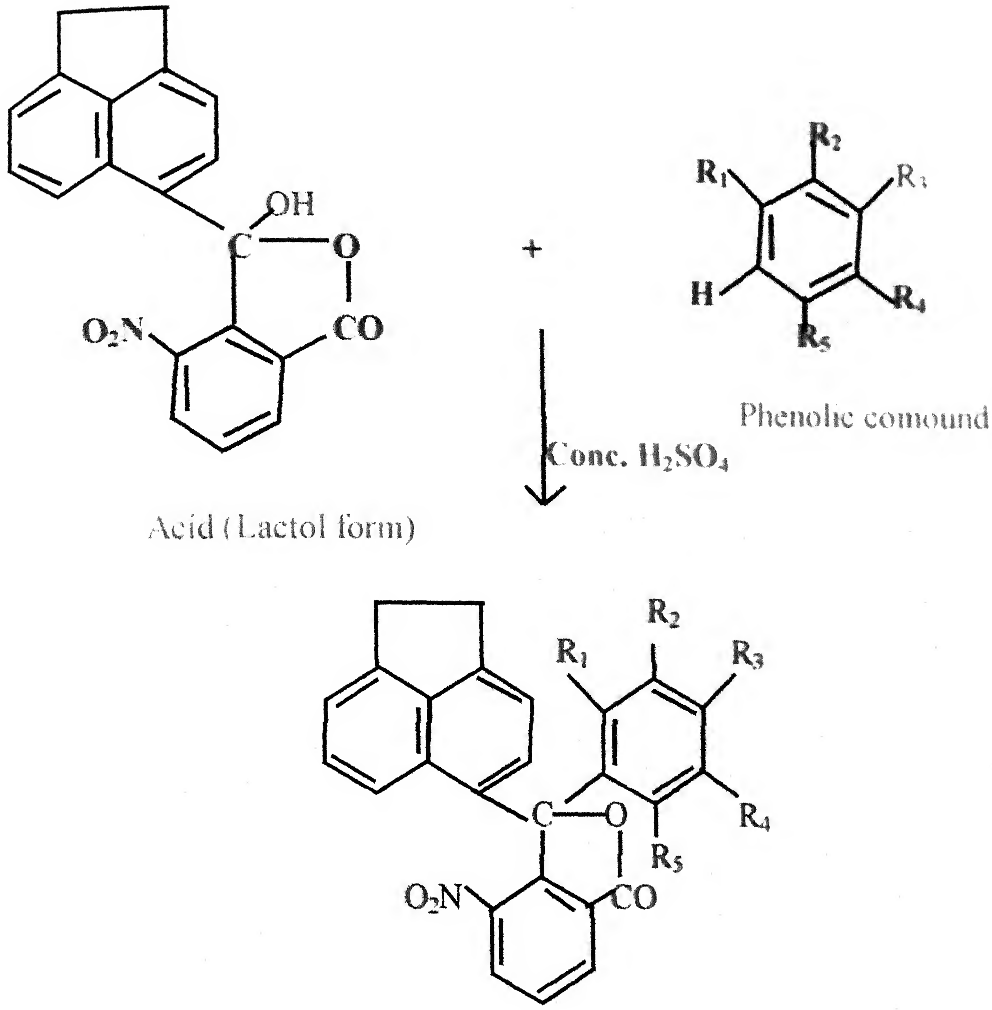
Anal. for	$C_{20}H_{13}NO_5$	(molecular weight 347)
Calc.	C, 69.16; H, 3.75; N, 4.03;	
Found	C, 69.12; H, 3.70; N, 4.01;	

C.4.1. PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

The acetyl derivative of the acid (1.0g) was prepared and purified in a similar way as the acetyl derivative C.1.1 chapter V, yield 0.70g, m.p 180-182^{0}C. It is soluble in chloroform, acetone, ethanol and acetic acid.

Anal. for	$C_{20}H_{12}NO_5(COCH_3)$	(molecular weight 389)
Calc.	C, 61.70; H, 3.08; N,5.60; Acetyl, 11.05;	
Found	C, 61.48; H, 3.04; N, 5.58; Acetyl, 11.02;	

The dye prepared from the acid may be represented by the following general formula:



Dye molecule

C.4.2 3-Acenaphthyl phenol nitro phthal-as-ein :
R_1=R_2=R_4=R_5=H ; R_3=OH

C.4.3 3-Acenaphthyl resorcinol nitro phthal-as-ein :
R_2=R_4 =R_5=H ; R_1= R_3=OH

C.4.4 3-Acenaphthyl catechol nitro phthal-as-ein :
R_3=R_4 =R_5=H ; R_1= R_2=OH

C.4.5 3-Acenaphthyl hydroquinone nitro phthal-as-ein :
R_2=R3 =R_5=H ; R_1= R_4=OH

C.4.6 3-Acenaphthyl pyrogallol nitro phthal-as-ein :
$R_4=R_5=H$; $R_1= R_2= R_3=OH$

C.4.7 3-Acenaphthyl phloroglucinol nitro phthal-as-ein :
$R_2=R_4=H$; $R_1= R_3= R_5=OH$

C.4.8 3-Acenaphthyl diacetyl resorcinol nitro phthal-as-ein :
$R_2=R_4= R_5=H$; $R_1= R_3= R_5=OCOCH_3$

C.4.9 3-Acenaphthyl dibromo resorcinol phthal-as-ein :
$R_5=H$; $R_2= R_4=Br$; $R_1=R_3=OH$

C.4.2 PREPARTION OF (3-ACENAPHTHYL) PHENOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (3.0g) and phenol (1.5g) in presence of 5-6 drops of concentrated sulphuric acid. The heating was carried out for eight hours at 150-165^{0}C, till brittle mass on cooling was obtained. Excess of phenol was removed by steam distillation. The isolation and purification of the dye were done in the same manner as described in case of other phenol phthal-as-ein, yield 1.6g.

The grey coloured dye m.p 115-117^{0}C gives light yellow colour in ethanol which turns into pink on adding a drop of alkali. With strong alkali it gives pinkish red colour.

Anal. for	: $C_{26}H_{17}NO_5$ (molecular weight 423)
Calc.	: C, 73.76; H, 4.02; N, 3.31;
Found	: C, 73.64; H, 4.00; N, 3.28;

C.4.3 PREPARATION OF (3-ACENAPHTHYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (3.0g) and resorcinol (3.0g) by using 6-8 drops of concentrated sulphuric acid as condensing agent. Heating was continued for four hours at 140-150^{0}C , till brittle mass was obtained on cooling. The isolation and purification of the dye were done in the same manner as in case of other resorcinol dyes, yield 2.5g.

Red coloured micro crystalline dye has, m.p. 315-317^{0}C. Its ethanolic solution is yellow in colour which turns into yellowish orange with green fluorescence on addition of a drop of alkali. In strong basic medium it gives yellowish orange colour with intensified green fluorescence.

Anal. for : $C_{26}H_{17}NO_6$ (molecular weight 439)

Calc. : C, 71.07; H, 3.87; N, 3.19;

Found : C, 70.82; H, 3.84; N, 3.17;

C.4.4 PREPARATION OF (3-ACENAPHTHYL) CATECHOL NITRO PHTHAL-AS-EIN:

The dye was prepared by taking the acid (1.5g) and catechol 1.0g and 5-6 drops of conc. H_2SO_4 exactly with the same manner as C.1.4 chapter V. The isolation and purification were also done in identical manner, yield 0.8g.

Dark brown coloured dye has m.p >300^{0}C. Its ethanolic solution is brown in colour which turns into bluish green on addition of alkali.

Anal. for : $C_{26}H_{17}NO_6$ (molecular weight 439)

Calc. : C, 71.07; H, 3.87; N, 3.19;

Found : C, 70.82; H, 3.84; N, 3.17;

C.4.5 PREPARATION OF (3-ACENAPHTHYL) HYDROQUINONE NITRO PHTHAL-AS-EIN:

The dye was prepared, isolated & purified exactly as C.4.3 by taking approximate quantity of acid and hydroquinone, yield 50%.

The dark brown powdery dye has m.p. 202-204^{0}C. Its ethanolic solution is brownish red in colour which turns into purple on addition of alkali.

Anal. for : $C_{26}H_{17}NO_6$ (molecular weight 439)

Calc. : C, 71.07; H, 3.87; N, 3.19;

Found : C, 70.05; H, 3.85; N, 3.16;

C.4.6 PREPARATION OF (3-ACENAPHTHYL) PYROGALLOL NITRO PHTHAL-AS-EIN:

The dye was prepared isolated and purified by taking pyrogallol (1.5g) and acid (1.0g) in a similar manner as C.4.3, Yield (0.8g)

The shinning black, dye has m.p 215-217^{0}C. Its ethanolic solution is reddish brown which becomes violet on adding a drop of alkali. In strong basic medium, it shows blue-black colour.

Anal. for	: $C_{26}H_{17}NO_7$	(molecular weight 455)
Calc.	: C, 68.57; H, 3.74; N, 3.08;	
Found	: C, 68.42; H, 3.72; N, 3.04;	

C.4.7 PREPARATION OF (3-ACENAPHTHYL) PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

The dye was prepared, isolated and purified by a similar method as C.4.3. Yield 0.9g.The light brown coloured dye has m.p 240^{0}C (decomp.) . It gives light brown colour with ethanol, which becomes dark brown on adding a drop of alkali. In strong basic medium it gives dark brown colour.

Anal. for	: $C_{26}H_{17}NO_7$	(molecular weight 455)
Calc.	: C, 68.57; H, 3.74; N, 3.08;	
Found	: C, 68.50; H, 3.72; N, 3.04;	

C.4.8 ACETYLATION OF (3-ACENAPHTHYL) RESORCINOL NITRO PHTHAL-AS-EIN:

[3-Acenaphthyl diacetyl resorcinol nitro phthal-as-ein]

The dye 3-acenaphthyl resorcinol nitro phthal-as-ein was acetylated in a similar manner as C.1.8. The crude yellowish white product was treated with animal charcoal & crystallized from aqueous ethanol in presence of 2, 3 drops of acetic acid, Yield 60%.

The acetylated product is yellowish white, amorphous in nature, m.p 146-148^{0}C. It is soluble in ethanol, acetone and acetic acid.

Anal. for	: $C_{26}H_{15}NO_6(COCH_3)_2$	(molecular weight 523)
Calc.	: C, 59.66; H, 2.87; N,2.68; Acetyl, 16.44;	
Found	: C, 59.52; H, 2.84; N, 2.62; Acetyl, 16.40;	

C.4.9. BROMINATION OF (3-ACENAPHTHYL) RESORCINOL PHTHAL-AS-EIN:

[3-Acenaphthyl dibromo resorcinol nitro phthal-as-ein]

The dibromo derivative of the dye (3-acenapthayl resorcinol nitro phthal-as-ein) was prepared, purified and crystallized in a similar manner as described in the case of C.1.9 chapter V, yield 60%.

The brick red microcrystalline dye has m.p 130-132 ^{0}C Its ethanolic solution is yellow in colour which turns into yellowish orange with green fluorescence on adding a drop of alkali. In strong basic medium it gives deep red colour

Anal. For	: $C_{26}H_{15}Br_2NO_6$ (molecular weight 597)
Calc.	: Br, 26.80;
Found	: Br , 26.65

C.4.10 CAUSTIC POTASH TREATMENT OF (3-ACENAPHTHYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye was subjected to caustic potash treatment in a similar manner as C.1.10 chapterV. The following three residues were obtained.

Residue I:

It was identified to be the unreacted residual dye from its colour reactions confirmed by mixed melting point determination.

Residue II:

The yellowish white compound, m.p208-210^{0}C , gave the usual test of a carboxyl group and was identified as 2 (3' acenaphthoyl) 3-nitro benzoic acid & was confirmed by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Residue III:

The brownish red residue was purified & was identified to be resorcinol from its colour reactions & confirmed by mixed melting point determination with the authentic sample.

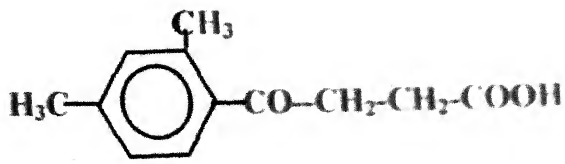
Bromination , acetylation & caustic potash fusion of the dye was shown in chart G chapter II.

CHAPTER

SIX

EXPERIMENTAL-D

DYES DERIVED FROM β-(2,4- DIMETHYL BENZOYL) PROPIONIC ACID:



D.1 Preparation of β-(2,4-dimethyl benzoyl) propionic acid.

The acid was prepared by carrying out Frieded-Crafts reaction between metaxylene (dry AR 80ml) and succinic anhydride (10.0g about 0.1 mole) in presence of anhydrous aluminium chloride (27.0g about 0.2 mole) as catalyst. The acid was isolated as the acid A.1chapter III yield was 16.0g. It was washed well with cold water, dried and crystallised from benzene/petroleum ether. The white crystals, of the acid m.p. 101-103^0 C are soluble in benzene, ether, acetone and chloroform.

Anal. For.	: $C_{12}H_{14}O_3$ (mol. wt. 206)
Calc.	: C, 69.90; H, 6.80;
Found	: C, 69.71; H, 6.75;

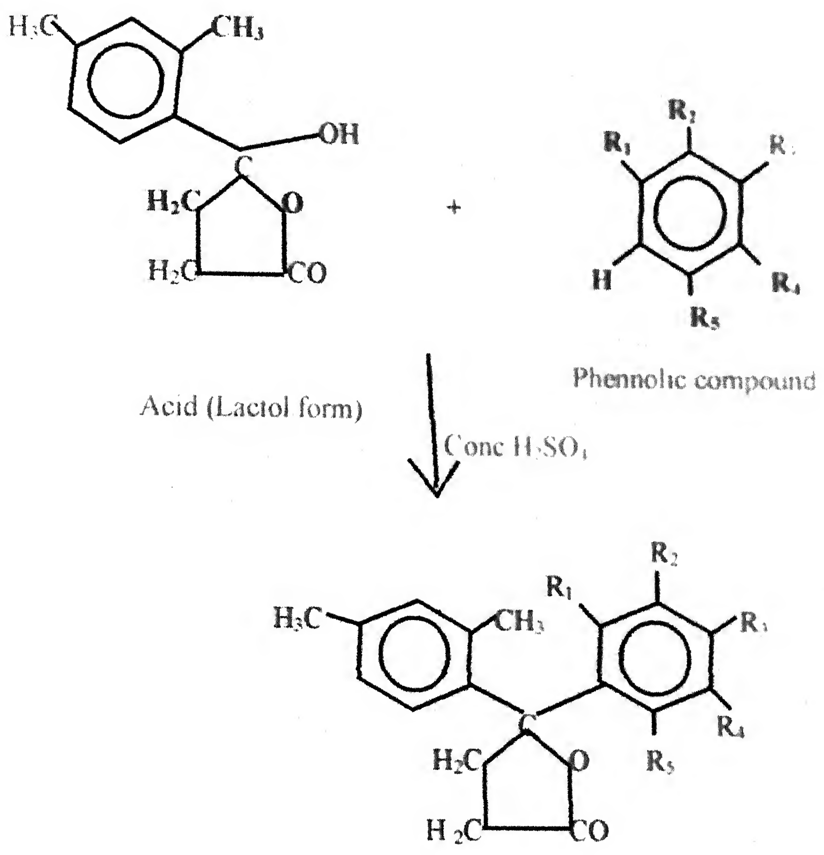
D.1.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

The β-(2, 4-dimethyl benzoyl) propionic acid (1.0g) was acetylated and the acetyl derivative was isolated and purified exactly in an identical manner as A 1.1 chapter III yield 0.65g.

The yellowish brown acetylated product has m.p. 94-96^{0}C. It is soluble in alcohol, chloroform and acetic acid.

Anal. For.	: $C_{14}H_{16}O_4$ or $C_{12}H_{13}O_3$ $(COCH_3)$ (mol. wt. 284)
Calc.	: C, 67.74; H, 6.45; acetyl. 17.34;
Found	: C, 67.54; H, 6.41; acetyl, 17.28;

The dyes prepared from the acid may be represented by the following structure:



Dye molecule

D.1.2 (2, 4-dimethyl phenyl) phenol succin-as-ein.
$R_1 = R_2 = R_4 = R_5 = H, R_3 = OH$

D.1.3 (2, 4-dimethyl phenyl) resorcinol succin-as-ein.
$R_2 = R_4 = R_5 = H,\ R_1 = R_3 = OH$

D.1.4 (2, 4-dimethyl phenyl) catechol succin-as-ein.
$R_3 = R_4 = R_5 = H,\ R_1 = R_2 = OH$

D.1.5 (2, 4-dimethyl phenyl) hydroquinone succin-as-ein.
$R_2 = R_3 = R_5 = H,\ R_1 = R_4 = OH$

D.1.6 (2, 4-dimethyl phenyl) pyrogallol succin-as-ein.
$R_4 = R_5 = H,\ R_1 = R_2 = R_3 = OH$

D.1.7 (2, 4-dimethyl phenyl) phloroglucinol succin-as-ein.

$R_2 = R_4 = H,\ R_1 = R_3 = R_5 = OH$

D.1.8 (2, 4-dimethyl phenyl) diacetyl resorcinol succin-as-ein.

$R_2 = R_4 = R_5 = H,\ R_1 = R_3 = O.COCH_3$

D.1.9 (2, 4-dimethyl phenyl) dibromo resorcinol succin-as-ein.

$R_5 = H, R_2 = R_4 = Br;\ R_1 = R_3 = OH$

D.1.2 PREPARATION OF (2, 4-DIMETHYL PHENYL) PHENOL SUCCIN-AS-EIN :

The dye was prepared by condensing the homogeneous mixture of the acid (2.0g) and phenol (1.5g) at 160-170^{0}C for four hours in presence of 4-6 drops of conc. sulphuric acid. The isolation and purification was carried out in the same way as A 1.2 chapter III, yield 1.5g.

The dark brown dye having m.p. 148-149^{0}C, dissolve in ethanol giving yellow colour, which turns into brown on adding a drop of alkali.

Anal. For.	: $C_{18}H_{18}O_3$ (mol. wt. 282)
Calc.	: C, 76.60; H, 6.38;
Found	: C, 76.39; H, 6.34;

D.1.3 PREPARATION OF (2, 4-DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN :

It was prepared by carrying out the condensation of the acid (3.0g) and resorcinol (2.0g) in an oil bath at 130-140^{0}C for four hours, in presence of 5-6 drops of conc. sulpuric acid. The dye was isolated and purified in a similar manner as A.1.3 chapter III.

The yellowish brown dye having m.p. 220-222^{0}C, is soluble in benzene, chloroform, alcohol, and acetic acid. It gives golden yellow colour in ethanol which changes into wine red with green fluorescence on adding a drop of alkali.

Anal. For.	: $C_{18}H_{18}O_4$ (mol. wt. 298)
Calc.	: C, 72.48; H, 6.04;

Found : C, 72.30; H, 6.01;

D.1.4 PREPARATION OF (2,4 DIMETHYL PHENYL) CATECHOL SUCCIN-AS-EIN:

It was prepared by heating the intimate mixture of the acid (1.5g) and catechol (1.0g) in an oil bath at 120-130^{0}C in presence of conc. Sulphuric acid 4-6 drops for about three hours. The isolation and purification were done in a similar manner as in case of A.1.3 chapter III, yield 0.8g.

The black coloured dye, m.p above 360^{0}C, gives light brown colour with ethanol which darkness on adding a drop of alkali.

Anal. For. : $C_{18}H_{18}O_4$ (mol. wt. 298)

Calc. : C, 72.48; H, 6.04;

Found : C, 72.27; H, 6.02;

D.1.5 PREPARATION OF (2,4 DIMETHYL PHENYL) HYDROQUINONE SUCCIN-AS-EIN:

The mixture of the acid (1.0g) hydroquinone (1.0g) and few drops of conc. Sulphuric acid, was heated in a oil bath at 160-180^{0}C, for about three and half hours. The isolation and purification of the dye were carried out in a same manner as in the case of A.1.3 chapter III, yield 1.2g.

The black dye having m.p. 240^{0}C gives light brown colour in ethanol which darkenes on addition of alkali.

Anal. For. : $C_{18}H_{18}O_4$ (mol. wt. 298)

Calc. : C, 72.48; H, 6.04;

Found : C, 72.29; H, 6.01;

D.1.6. PREPARATION OF (2,4 DIMETHYL PHENYL) PYROGALLOL SUCCIN-AS-EIN:

The condensation of the intimate mixture of acid (1.0g) pyrogallol (1.2g) was carried out in presence of 4-8 drops of conc. Sulphuric acid at 160-180^{0}C for four hours. Isolation and purification of the dye were done as in case of A.1.3 chapter III, yield 1.0g.

The black coloured dye m.p. above 360^{0}C, is soluble in acetone, ethanol, methanol and acetic acid. Its ethanolic solution is crimson which gives dark red colour adding a drop of alkali.

Anal. For. : $C_{18}H_{18}O_5$ (mol. wt. 314)

Calc. : C, 68..79; H, 5.73;

Found : C, 68.62; H, 5.69;

D.1.7. PREPARATION OF (2,4 DIMETHYL PHENYL) PHLOROGLUCINOL SUCCIN-AS-EIN:

The dye was prepared isolated and purified identically as described in the case of A.1.3 chapter III. Acid (1.5g) phloroglucinol (1.5g) and 4-8 drops of conc.sulphuric acid were heated at 190-200^{0}C for about four hours, yield 1.5g.

The dark brown dye decomposed at 180^{0}C, is soluble in acetone, ethanol, methanol and acetic acid.

Anal. For. : $C_{18}H_{18}O_5$ (mol. wt. 314)

Calc. : C, 68..79; H, 5.73;

Found : C, 68.58; H, 5.70;

D.1.8. ACETYLATION OF (2,4-DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:

[(2,4-dimethyl phenyl) diacetyl resorcinol succin-as-ein]

The dye (2,4-dimethyl phenyl) resorcinol succin-as-ein (1.0g) was acetylated, isolated and purified identically in a similar manner as A.1.8 chapter III, yield (0.70g).

The acetylated brown product having m.p. 320-322^{0}C, is soluble in benzene, ether, acetone, methanol and chloroform.

Anal. For. : $C_{22}H_{22}O_6$ or $C_{18}H_{16}O_4$ (OC.CH_3) (Mol.wt. 382)

Calc. : C, 69.11; H, 5.76; acety, 22.51;

Found : C, 68.91; H, 5.72; acetyl, 22.40;

D.1.9 BROMINATION OF (2,4-DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN :

[(2,4-dimethyl phenyl) dibromo resorcinol succin-as-ein]

The dye (2,4-dimethyl phenyl) resorcinol succin-as-ein (1.0g) was brominated and the product was extracted and purified in the similar way as described in the bromination of A.1.9 chapter III, yield 0.85g.

The dark brown dye, m.p. 150-151^{0}C, is soluble in benzene, ether, acetone, methanol and chloroform.

Anal. For. : $C_{18}H_{16}Br_2O_4$ (mol.wt.456)

Calc. : Br, 35.09; Found : Br, 35. 00;

D.1.10 CAUSTIC POTASH TREATMENT OF (2,4-DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:

Potash hydroxide fusion of the dye (1.0g) was carried out in a similar manner as in case of A.1.10 chapter III. Following three residues obtained as identified.

Identification of Residue I:

Residue (I) was identified as unreacted residual dye from its colour reactions. It was further confirmed by mixed melting point determination with the original dye.

Identification of Residue II:

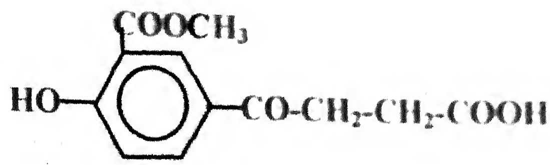
It was found to be acidic, m.p. 101-103^{0}C, gave positive test for carboxylic acid and was identified to be (2,4-dimethyl benzoyl) propionic acid and confirmed by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Identification of Residue III:

The compound, m.p 110^{0}C gave violet blue colour with ferric chloride and responded fluorescene test with phthalic anhydride. It reduced Felhling's solution and Tollen's reagent. The melting point didn't show any depression when mixed with the authentic sample of resorcinol. It was inferred to be resorcinol.

The acetylation, bromination and caustic potash fusion of the resorcinol dye are given in chart B, chapter II.

DYES DERIVED FROM β-(3-CARBMETHOXY 4-HYDROXY BENZOYL) PROPIONIC ACID



D.2 preparation of β-(3 Carmethoxy 4-hydroxy benzoyl) propionic acid:

The acid was prepared and isolated in the same manner as the preparation of other γ-keto acids by carrying out Friedel Craft reaction reaction between methyl salicylate (dry AR, 80ml) and succinic anhydride (10.0g, about 0.1 mole) in presence of anhydrous aluminum chloride (27.0g, about 0.2 mole) as the catalyst. The crude acid was washed well with cold water, dried and crystallized from benzene/petroleum, ether, melting point 193-94^{0}C.yield 15.0g.

The white crystalline acid is soluble in ether, benzene, chloroform, acetone, methanol and acetic acid.

Anal. For.	: $C_{12}H_{12}O_6$ (mol. wt. 252)
Calc.	: C, 57.14; H, 4.76;
Found	: C, 57.07; H, 4.72;

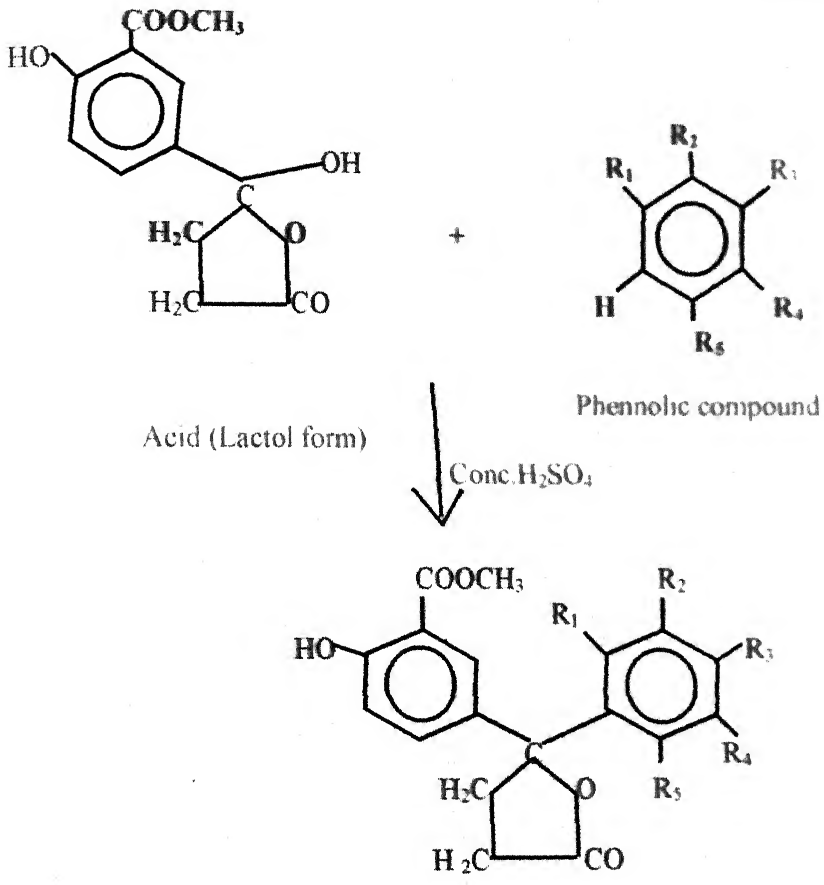
D.2.1 PREPARATION OF THE ACETYL DERIVATIVE OF THE ACID:

One gram of the acid and three grams of fused sodium acetate were refluxed with 15ml of freshly distilled acetic anhydride at 130-140^{0}C for three and half hours. The hot contents were poured in a breaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of blackish brown solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal. It was filtered while hot. It was finally crystallized from acetone, yield 0.60g, m.p>360^{0}C. It is soluble in acetone, ethanol and acetic acid.

Anal. For.	: $C_{14}H_{14}O_7$ or $C_{12}H_{11}O_6(COCH_3)$ (mol. wt. 294)

Calc.	: C, 57.14; H, 4.76; acetyl. 14.63;
Found	: C, 57.01; H, 4.72; acetyl, 14.60;

The dyes derived from the acid can be conveniently represented by the following general formula:



Dye molecule

D.2.2 (3-carbmethoxy 4-hydroxy) phenol succin-as-ein.
$R_1 = R_2 = R_4 = R_5 = H, R_3 = OH$

D.2.3 (3-carbmethoxy 4-hydroxy) resorcinol succin-as-ein.
$R_2 = R_4 = R_5 = H,\ R_1 = R_3 = OH$

D.2.4 (3-carbmethoxy 4-hydroxy) catechol succin-as-ein.
$R_3 = R_4 = R_5 = H,\ R_1 = R_2 = OH$

D.2.5 (3-carbmethoxy 4-hydroxy) hydroquinone succin-as-ein.
$R_2 = R_3 = R_5 = H,\ R_1 = R_4 = OH$

D.2.6 (3-carbmethoxy 4-hydroxy) pyrogallol succin-as-ein.
$R_4 = R_5 = H,\ R_1 = R_2 = R_3 = OH$

D.2.7 (3-carbmethoxy 4-hydroxy) phlorolucinol succin-as-ein.
$R_2 = R_4 = H,\ R_1 = R_3 = R_5 = OH$

D.2.8 (3-carbmethoxy 4-hydroxy) diacetyl resorcinol succin-as-ein.
$R_2 = R_4 = R_5 = H,\ R_1 = R_3 = O.COCH_3$

D.2.9 (3-carbmethoxy 4-hydroxy) dibromo resorcinol succin-as-ein.
$R_5 = H, R_1 = R_3 = OH;\ R_2 = R_4 = Br$

D.2.2 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY) PHENOL SUCCIN-AS-EIN:

An intimate mixture of 1.5g of the acid and 1.0g of phenol (slight excess than molecular proportion) as taken in a hard boiling tube and heated in an oil bath to make the contents homogenous. 4-6 drops of conc. Sulphuric acid were then added and heating was continued at 160-170^{0}C for six hours till the molten mass in the tube becomes brittle on cooling. The condensed mass was taken out from the tube and subjected to steam distillation to remove the excess of phenol. The brownish black mass left in the flask was powdered and extracted with 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured was purified by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallized from rectified spirit and dried in vacuum desiccator , yield 1.8g, m.p 102-103^{0}C.

The blackish brown dye is soluble in ethanol, acetone, ether and acetic acid. The ethanolic solution is almost yellowish brown in colour and on adding a drop of an alkali, it becomes pinkish red in colour.

The purity of the dye was tested by paper chromatography adopting the same technique as in other phenolic phtahl-as-eins.

Anal. For	: $C_{18}H_{16}O_6$ (mol.wt. 328)
Calc.	: C, 65.85; H, 4.88;
Found	: C, 65.78; H, 4.84;

D.2.3 PREPARATION OF (3-CARBMETHOXY 4–HYDROXY PHENYL) RESORCINOL-SUCCIN-AS-EIN :

A well ground mixture of the acid (3.5g) and resorcinol (2.0g) was heated in an oil bath at 130°C to make it homogeneous. 6-8 drops of concentrated sulphuric acid were added and stirred well. The heating was continued at 150-170°C for about four hours till the melt became hard and brittle on cooling. The condensed mass was crushed and washed well with water to remove excess of resorcinol. It was extracted with 2% solution of aqueous caustic soda solution and filtered. The dye was precipitated as a reddish brown solid from the filtrate by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 80° C and then in a vacuum desiccator, yield 2.5g. The reddish orange crystalline dye has a m.p. 86-88°C. The ethanolic solution is light red in colour that on addition of a drop of an alkali changes into yellowish orange with green fluorescence. The green fluorescence darkens on addition of a 2% solution of caustic soda.

Anal. For : $C_{18}H_{16}O_7$ (mol.wt. 344)

Calc. : C, 62.79; H, 4.65;

Found : C, 62.68; H, 4.63;

D.2.4 PREPARATION OF (3-CARBMEHOXY 4-HYDROXY PHENYL) CATECHOL SUCCIN-AS-EIN :

An intimate mixture of the acid (1.5g) and catechol (1.0g) was heated on an oil bath at 100°C to make it homogenous. 4-6 drops of concentrated sulphuric acid were added and stirred well. Heating was continued at 145-170°C for three hours till a hard brittle mass was obtained on cooling. The isolation and purification was done as in the case of D.2.3 yield 1.0g.

The dye is dark brown crystalline soda solution, m.p. 116-118°C. It ethanolic solution is brown in colour. With 2% caustic soda solution, it gives black colour.

Anal. For : $C_{18}H_{16}O_7$ (mol.wt. 344)

Calc. : C, 62.79; H, 4.65;

Found : C, 62.67; H, 4.62;

D.2.5 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) HYDROQUINONE SUCCIN-AS-EIN :

An intimate mixture of the acid (1.0g) and hydroquinone (1.0g) was heated

on an oil bath in presence of 6-8 drops of concentrated sulpuric acid at 170-190° C for four hours. The isolation and the purification of the dye were carried out in a manner similar to that described in section D.2.3, yield 1.2g.

The black shining dye has a m.p. 242-244°C. The ethanolic solution is light brown which turns into brownish red colour on addition of a drop of an alkali.

Anal. For	: $C_{18}H_{16}O_7$ (mol.wt. 344)
Calc.	: C, 62.79; H, 4.65;
Found	: C, 62.68; H, 4.63;

D.2.6 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) PYROGALLOL SUCCIN-AS-EIN :

The condensation of an intimate mixture of the acid (1.5g) and pyrogallol (1.0g) was carried out by heating the mixture with 6-8 drops with concentrated sulphuric acid in an oil bath at 160-180°C for about four hours till a brittle mass was obtained on cooling. The isolation and purification were done as in the case of D.2.3 section, yield 1.0g.

The dye is black and crystalline in nature, m.p. >360°C. Its ethanolic solution is blackish brown which gives black colour on addition of a drop of an alkali.

Anal. For	: $C_{18}H_{16}O_8$ (mol.wt. 360)
Calc.	: C, 60.00; H, 4.44;
Found	: C, 59.86; H, 4.40;

D.2.7 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) PHLOROGLUCINOL SUCCIN-AS-EIN :

The acid (1.5g) and phloroglucinol (1.0g) were mixed intimately and heated on an oil bath to make it homogeneous. A few drops of concentrated sulphuric acid were added and heating carried out at 180-200°C for four hours. The isolation and purification were done as in the case D.2.3, yield 0.8g.

It is a yellowish red dye, which decomposes at 300°C without melting. It gives reddish brown colour in ethanol, which turns into red colour on addition of a drop of an alkali.

Anal. For : $C_{18}H_{16}O_8$ (mol.wt. 360)

Calc. : C, 60.00; H, 4.44;

Found : C, 59.84; H, 4.42;

D.2.8 PREPARAION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) DIACTYL RESORCINOL SUCCIN-AS-EIN :

[(Acetylation of (3-carbmethoxy 4-hydroxy phenyl) resorcinol succin-as-ein].

The dye (3-carbmethoxy 4-hydroxy phenyl) resorcinol succin-as-ein (1.0g) and fused sodium acetate (3.0g) with 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask with an air condenser. The contents were refluxed at 130-140^{0}C for about three and half-hours. The hot contents were then slowly and gradually poured into a beaker containing a slush of ice and water accompanied by constant stirring. It was left overnight whereupon a brown solid settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallized from aqueous alcohol and a little acetic acid. It was dried in oven at 80^{0}C and then over phosphorous pentoxide under reduced pressure, yield 0.8g.

The crystalline brown acetylated product, m.p. 82-84^{0}C is soluble in ethanol, acetone and acetic acid. Its ethanolic solution is light yellow, which turns into brown on addition of a drop of an alkali.

Anal. For : $C_{22}H_{20}O_9$ or $C_{18}H_{14}O_7(OC.CH_3)_2$ (mol.wt. 428)

Calc. : C, 61.52; H, 4.67; acetyl. 20.09;

Found : C, 61.52; H, 4.62; acetyl. 20.03;

D.2.9 PREPARATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) DIBROMO RESORCINOL SUCCIN-AS-EIN :

[Bromination of (3-carbmethoxy 4-hydroxy phenyl)-resorcinol-succin-as-ein].

(1.0g)of resorcinol dye dissolved in minimum quantity of glacial acetic acid. 10.0g ml of a 10% solution of bromine in glacial acetic acid was added to the solution of the dye. The flask was fitted with an air condenser and contents were refluxed at 130-140^0 C for an hour. The product was cooled and diluted with a minimum quantity of distilled water. A brown powder settled down. It was filtered

and washed well with water containing acetic acid and finally with hot water to remove an excess of bromine. It was dissolved in dilute aqueous caustic soda solution and filtered. The filtrate gave the bromo derivative of the dye on gradual slow addition of dilute hydrochoric acid. The crude brominated dye was finally purified by crystallization from aqueous alcohol and dried at 80°C in an oven and then in a vacuum desiccator, yield 0.8g.

The brown coloured amorphous dye, m.p.>360°C, gives yellowish red colour in ethanol which turns into violet on addition of an alkali.

Anal. For	: $C_{18}H_{14}O_7Br_2$ (mol.wt. 502)
Calc.	: C, 43.03; H, 2.79; Br, 31.87;
Found	: C, 42.98; H, 2.76; acetyl. 31.82;

D.2.10 CAUSTIC POTASH TREATMENT OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL SUCCIN-AS-EIN:

The potassium hydroxide fusion of the dye was carried out as in the case of other resorcinol succin-as-eins. As a result three residues were obtained.

Residue I:

it was identified as the unreacted residual dye giving all colour reactions of the dye itself. It was confirmed by mixed melting point determination with the original dye.

Residue II:

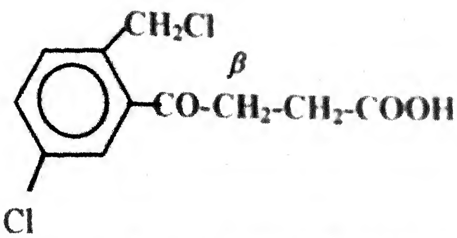
The compound, m.p193-94°C gave the usual test for the presence of the carboxylic group and was identified as β-(3- carbmethoxy 4-hydroxy benzoyl) propionic acid. It was confirmed to be the acid by mixed melting point determination and superimposition of the IR spectra with the authentic sample.

Residue III:

The purified substance melted at 109-110°C. It gave violet colour with ferric chloride solution and also reduced Tollen's reagent and Fehling solution. It responded to fluorescence test with phthalic anhydride. On the basis of those observations, the residue III identified as resorcinol. It was confirmed to be so by mixed melting point determination with an authentic sample of resorcinol.

Acetylation, bromination and caustic potash treatment reactions of the dye have been depicted in chart D, chapter II.

DYES DERIVED FROM β-(5-CHLORO 2-CHLORO METHYL BENZOYL) PROPIONIC ACID



D.3.PREPARATION OF β-(5-CHLORO 2-CHLOROMETHYL BENZOYL) PROPIONIC ACID:

The acid was prepared and isolated in the same manner as the preparation of other γ-keto acids by carrying out Friedel Craft reaction between 4-chloro benzyl chloride (dry AR, 80ml) and succinic anhydride (10.0g, about 0.1 mole) in presence of anhydrous aluminum chloride (27.0g, about 0.2 mole) as the catalyst. The crude acid was washed well with cold water, dried and crystallized from benzene/petroleum, ether, melting point 158-60°C yield 15.0g.

The white crystalline acid is soluble in ether, benzene, chloroform, acetone, methanol and acetic acid.

Anal. For.	: $C_{11}H_{10}Cl_2O_3$ (mol. wt. 271)
Calc.	: C, 48.71; H, 3.69; Cl, 26.20;
Found	: C, 48.66; H, 3.67; Cl, 26.18;

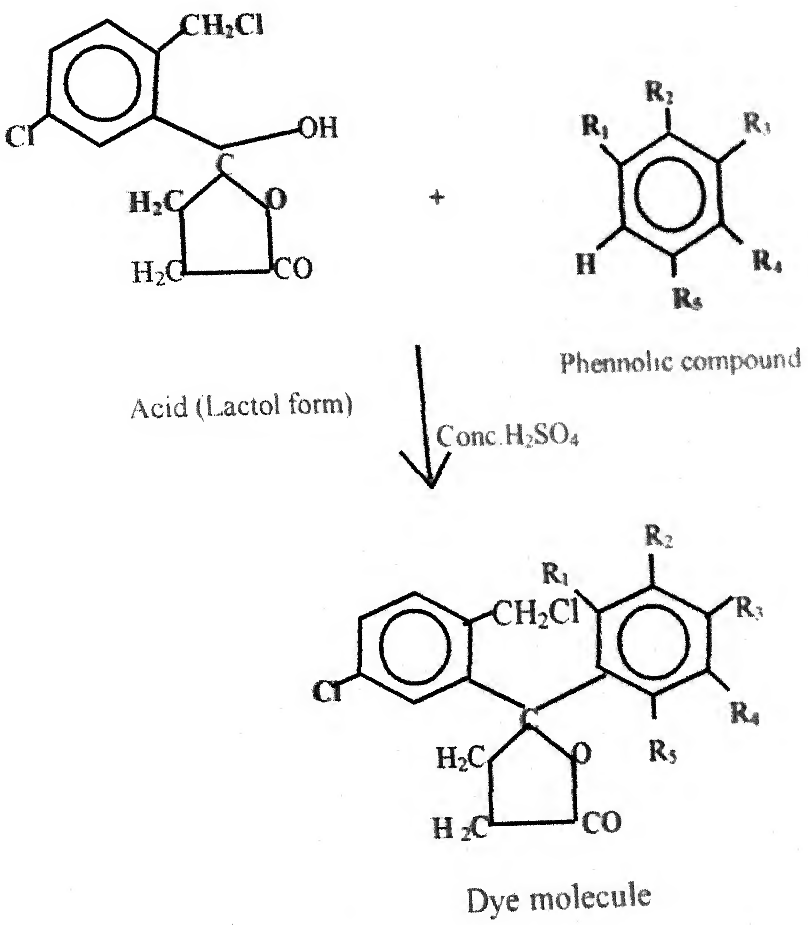
D.3.1 PREPARATION OF THE ACETYL DERIVATIVE OF THE ACID:

One gram of the acid and three grams of fused sodium acetate were refluxed with 15ml of freshly distilled acetic anhydride at 135-140^{0}C for three and half hours. The hot contents were poured in a breaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of blackish brown solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal. It was filtered while hot. It was finally crystallized from acetone, yield 0.60g, m.p.186-87^{0}C.It is soluble in acetone, ethanol and acetic acid.

Anal. For.	: $C_{13}H_{12}Cl_2O_4$ or $C_{11}H_9Cl_2O_3(COCH_3)$ (mol. wt. 303)
Calc.	: C, 51.48; H, 3.96; Cl, 23.43; acetyl, 14.19;

Found : C, 51.24; H, 3.95; Cl, 23.40; acetyl,14.13;

The dyes derived from the acid can be conveniently represented by the following general formula:



D.3.2 (5-chloro 2-chloromethyl phenyl) phenol succin-as-ein.
$R_1 = R_2 = R_4 = R_5 = H, R_3 = OH$

D.3.3 (5-chloro 2-chloromethyl phenyl) resorcinol succin-as-ein.
$R_2 = R_4 = R_5 = H, \ R_1 = R_3 = OH$

D.3.4 (5-chloro 2-chloromethyl phenyl) catechol succin-as-ein.
$R_3 = R_4 = R_5 = H, \ R_1 = R_2 = OH$

D.3.5 (5-chloro 2-chloromethyl phenyl) hydroquinone succin-as-ein.
$R_2 = R_3 = R_5 = H, \ R_1 = R_4 = OH$

D.3.6 (5-chloro 2-chloromethyl phenyl) pyrogallol succin-as-ein.

$R_4 = R_5 = H, \; R_1 = R_2 = R_3 = OH$

D.3.7 (5-chloro 2-chloromethyl phenyl) phlorolucinol succin-as-ein.
$R_2 = R_4 = H, \; R_1 = R_3 = R_5 = OH$

D.3.8 (5-chloro 2-chloromethyl phenyl) diacetyl resorcinol succin-as-ein.
$R_2 = R_4 = R_5 = H, \; R_1 = R_3 = O.COCH_3$

D.3.9 (5-chloro 2-chloromethyl phenyl) dibromo resorcinol succin-as-ein.
$R_5 = H, R_1 = R_3 = OH; R_2 = R_4 = Br$

D.3.2 PREPARATION OF ~~(3-carbmethoxy 4 hydroxy)~~ (5-Chloro-2chloromethyl phenyl) PHENOL SUCCIN-AS-EIN:

An intimate mixture of 1.5g of the acid and 1.0g of phenol (slight excess than molecular proportion) as taken in a hard boiling tube and heated in an oil bath to make the contents homogenous. 4-6 drops of conc. Sulphuric acid were then added and heating was continued at 145-165^{0}C for six hours till the molten mass in the tube becomes brittle on cooling. The condensed mass was taken out from the tube and subjected to steam distillation to remove the excess of phenol. The brownish black mass left in the flask was powdered and extracted with 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured was purified by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallized from rectified spirit and dried in vacuum desiccator , yield 1.8g, m.p 101-103^{0}C.

The blackish brown dye is soluble in ethanol, acetone, ether and acetic acid. The ethanolic solution is almost yellowish brown in colour and on adding a drop of an alkali, it becomes pinkish red in colour.

The purity of the dye was tested by paper chromatography adopting the same technique as in other phenolic phtahl-as-eins.

Anal. For : $\cancel{C_{18}H_{16}O_6}$ $C_{17}H_{14}Cl_2O_3$ (mol.wt. ~~328~~ 337)

Calc. : C, ~~65.85~~ 60.53; H, ~~4.88~~ 4.15; Cl, 21.06

Found : C, ~~65.78~~ 60.40; H, ~~4.84~~ 4.13; Cl, 21.02

D.3.3 PREPARATION OF (~~3-CARBMETHOXY 4-HYDROXY~~ 5-chloro 2chloromethyl PHENYL) RESORCINOL-SUCCIN-AS-EIN :

A well ground mixture of the acid (3.5g) and resorcinol (2.0g) was heated in

an oil bath at 130^0 C to make it homogeneous. 6-8 drops of concentrated sulphuric acid were added and stirred well. The heating was continued at 150-170^{0}C for about four hours till the melt became hard and brittle on cooling. The condensed mass was crushed and washed well with water to remove excess of resorcinol. It was extracted with 2% solution of aqueous caustic soda solution and filtered. The dye was precipitated as a reddish brown solid from the filtrate by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 80^{0}C and then in a vacuum desiccator, yield 2.5g. The reddish orange crystalline dye has a m.p. 86-88^{0}C. The ethanolic solution is light red in colour that on addition of a drop of an alkali changes into yellowish orange green fluorescence. The green fluorescence darking on addition of a 2% solution of caustic soda.

Anal. For	: $C_{17}H_{14}Cl_2O_4$ (mol.wt. 353)
Calc.	: C, 57.79; H, 3.97; Cl, 20.11;
Found	: C, 57.69; H, 3.94; Cl, 20.09;

D.3.4 PREPARATION OF (5-CHLORO 2-CHLOROMETHYL PHENYL) CATECHOL SUCCIN-AS-EIN :

An intimate mixture of the acid (1.5g) and catechol (1.0g) was heated on an oil bath at 100^{0}C to make it homogenous. 2-4 drops of concentrated sulphuric acid were added and stirred well. Heating was continued at 130-145^{0}C for three hours till a hard brittle mass was obtained on cooling. The isolation and purification was done as in the case (5-chloro 2-chloromethyl phenyl) resorcinol succin-as-ein, yield 1.0g.

The dye is dark brown crystalline soda solution, m.p. 116-118^{0}C. It ethanolic solution is brown in colour. With 2% caustic soda solution, it gives black colour.

Anal. For	: $C_{17}H_{14}Cl_2O_4$ (mol.wt. 353)
Calc.	: C, 57.79; H, 3.97; Cl, 20.11;
Found	: C, 57.72; H, 3.93; Cl, 20.07;

D.3.5 PREPARATION OF (5-CHLORO 2-CHLOROMETHYL PHENYL) HYDROQUINONE SUCCIN-AS-EIN :

An intimate mixture of the acid (1.0g) and hydroquinone (1.0g) was heated on an oil bath at in presence of 4-6 drops of concentrated sulpuric acid at 170-

180°C for four hours. The isolation and the purification of the dye were carried out in a manner similar to that described in D.3.3, yield 1.0g.

The black shining dye has a m.p. 260-262°C. The ethanolic solution is light brown which turns into brownish red colour on addition of a drop of an alkali.

Anal. For	: $C_{17}H_{14}Cl_2O_4$ (mol.wt. 353)
Calc.	: C, 57.79; H, 3.97; Cl, 20.11;
Found	: C, 57.72; H, 3.93; Cl, 20.07;

D.3.6 PREPARATION OF (5-CHLORO 2-CHLORO METHYL PHENYL) PYROGALLOL SUCCIN-AS-EIN :

The condensation of an intimate mixture of the acid (1.5g) and pyrogallol (1.0g) was carried out by heating the mixture with 5-6 drops with concentrated sulphuric acid in an oil bath at 140-160° C for about four hours till a brittle mass was obtained on cooling. The isolation and purification was done as in the case D.3.3, yield 1.0g.

The dye is black and crystalline in nature, m.p. >360°C. Its ethanolic solution is blackish brown which gives black colour on addition of a drop of an alkali.

Anal. For	: $C_{17}H_{14}Cl_2O_5$ (mol.wt. 369)
Calc.	: C, 55.28; H, 3.79; Cl, 19.24;
Found	: C, 55.12; H, 3.74; Cl, 19.19;

D.3.7 PREPARATION OF (5-CHLORO 2-CHLOROMETHYL PHENYL) PHLOROGLUCINOL SUCCIN-AS-EIN :

The acid (1.5g) and phloroglucinol (1.0g) were mixed intimately and heated on an oil bath to make it homogeneous. A few drops of concentrated sulphuric acid were added and heating carried out at 180-190°C for four hours. The isolation and purification was done as in the case D.3.3, yield 0.9g.

It is a yellowish red dye, which decomposes at 300°C without melting. It gives reddish brown colour in ethanol, which turns into red colour on addition of a drop of an alkali.

Anal. For : $C_{17}H_{14}ClO_5$ **(mol.wt. 369)**

Calc. : C, 55.28; H, 3.79; Cl, 19.24;

Found : C, 55.19; H, 3.77; Cl, 19.20;

T

D.3.8 PREPARAION OF (5-CHLORO 2-CHLOROMETHYL PHENYL) DIACTYL RESORCINOL SUCCIN-AS-EIN :

[(Acetylation of (5-chloro 2-chloromethyl phenyl) resorcinol]. Succin-as-ein.

The dye (5-chloro 2-chloromethyl phenyl) resorcinol succin-as-ein (1.0g) and fused sodium acetate (3.0g) with 15ml of freshly distilled acetic anhydride was taken in a 50ml round bottom flask with an air condenser. The contents were refluxed at 120-140^{0}C for about three and half-hours. The hot contents were then slowly and gradually poured into a beaker containing a slush of ice and water accompanied by constant stirring. It was left overnight whereupon a brown solid settled down. It was filtrated, washed well and dried. The crude product was treated with animal charcoal and crystallized from aqueous alcohol and a little acetic acid. It was dried in oven at 50^{0}C and then over phosphorous pentoxide under reduced pressure, yield 0.7g.The crystalline brown acetylated product, m.p. 78-80^{0}C is soluble in ethanol, acetone and acetic acid. Its ethanolic solution is light yellow, which turns into brown on addition of a drop of an alkali.

Anal. For : $C_{21}H_{18}Cl_2O_6$ or $C_{17}H_{12}Cl_2O_4$ $(OC.CH_3)$ (mol.wt. 437)

Calc. : C, 57.67; H, 4.12; Cl, 16.25; Acetyl, 19.68;

57.52 4.09 16.21

Found : C, ~~55.19;~~ H, ~~3.77~~; Cl, ~~19.20~~; Acetyl, 19.59;

D.3.9 PREPARATION OF (5-CHLORO 2-CHLOROMETHYL PHENYL) DIBROMO RESORCINOL SUCCIN-AS-EIN :

[(Bromination of (5-chloro 2-chloromethyl phenyl) resorcinol]. succin-as-ein.

The dye, (5-chloro 2-chloromethyl phenyl)-resorcinol-succin (1.0g) dissolved in minimum quantity of glacial acetic acid. 10.0g ml of a 10% solution of bromine in glacial acetic acid was added to the solution of the dye. The flask was fitted with an air condenser and contents were refluxed at 120-130^{0}C for an hour. The product was cooled and diluted with a minimum quantity of distilled water. A brown powder settled down. It was filtered and washed well with water containing acetic acid and finally with hot water to remove an excess of bromine. It was dissolved in dilute aqueous caustic soda solution and filtered. The filtrate gave

the bromo derivative of the dye on gradual slow addition of dilute hydrochloric acid. The crude brominated dye was finally purified by crystallization from aqueous alcohol and dried at 80°C in an oven and then in a vacuum desiccator, yield 0.8g.

The brown coloured amorphous dye, m.p.>360°C, gives yellowish red colour in ethanol which turns into violot on addition of an alkali.

Anal. For	$C_{17}H_{12}Br_2Cl_2O_4$: ~~$C_{18}H_{14}$~~ (mol.wt. ~~502)~~ 511)
Calc.	: ~~C, 43.03~~; ~~H, 2.79~~; ~~Br, 31.87;~~ Br 31.31
Found	: ~~C, 42.98~~; ~~H, 2.76,~~ ~~acetyl. 31.~~82; Br 31.25

D.2.10 CAUSTIC POTASH TREATMENT OF (5-Chloro 2 Chloromethyl ~~3-CARBMETHOXY 4-HYDROXY~~ PHENYL) RESORCINOL SUCCIN-AS-EIN:

The potassium hydroxide fusion of the dye was carried out as in the case of other resorcinol succin-as-eins. As a result three residues were obtained.

Residue I:

It was identified as the unreacted residual dye giving all colour reactions of the dye itself. It was confirmed by mixed melting point determination with the original dye.

Residue II:

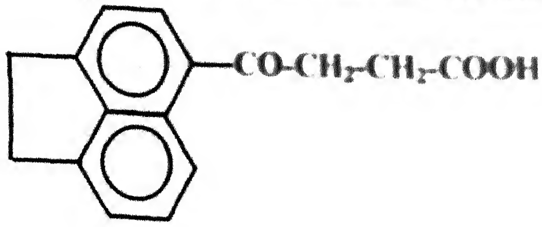
The compound, m.p 105-106°C gave the usual test for the presence of the carboxylic group and was identified as β-(5 Chloro 2 Chloromethyl ~~3 carbmethoxy 4 hydroxy~~ benzoyl) propionic acid. It was confirmed to be the acid by mixed melting point determination and superimposition of the IR spectra with the authentic sample.

Residue III:

The purified substance melted at 109-110°C. It gave violet colour with ferric chloride solution and also reduced Tollen's reagent and Fehling solution. It responded to fluorescence test with phthalic anhydride. On the basis of those observations, the residue III identified as resorcinol. It was confirmed to be so by mixed melting point determination with an authentic sample of resorcinol.

Acetylation, bromination and caustic potash treatment reactions of the dye have been placed in chart F, chapter II.

DYES DERIVED FROM β-(3-ACENAPTHOYL) PROPIONIC ACID



D.4 PREPARATION OF β-(3-ACENAPHTHOYL) PROPIONIC ACID :

The acid was prepared and isolated by carrying out Frieded-Crafts reaction between acenaphthene and succin anhydride in presence of anhydrous chloride in a similar manner as described for A.4 chapter III. The acid was crystallised from aqueous ethanol in the form of colourless needles, m.p. 216-218^{0}C. The acid is soluble in ethanol, ether, chloroform and sparingly soluble in benzene and insoluble in carbondisulphide.

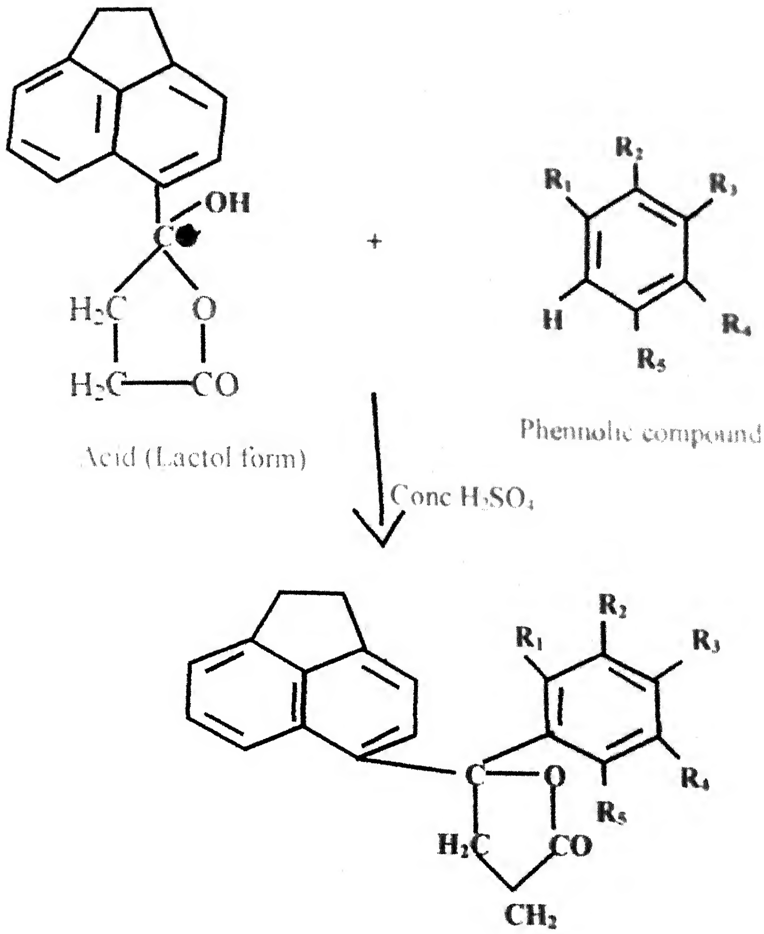
Anal. for.	: $C_{16}H_{14}O_3$ (mol. wt. 254)
Calc.	: C, 75.59; H, 5.51;
Found	: C, 75.54; H, 5.49;

D.4.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

The acetyl derivative of the acid was prepared and purified in similar way as the preparation of acetyl derivative of other γ -keto acids, yield o.70g. m.p. 170-172^{0}C. It is soluble in chloroform, acetone, ethanol and acetic acid.

Anal. for.	: $C_{16}H_{13}O_3$ ($COCH_3$) (mol. wt. 296)
Calc.	: C, 64.86; H, 4.39; acetyl. 16.32;
Found	: C, 64.75; H, 4.37; acetyl. 16.14;

The dyes prepared from the acid may be represented by the following general formula:



Dye molecule

D.4.2 (3-Acenaphthyl) phenol succin-as-ein :
$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

D.4.3 (3-Acenaphthyl) resorcinol succin-as-ein :
$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

D.4.4 (3-Acenaphthyl) catechol succin-as-ein :
$R_3 = R_4 = R_5 = H$; $R_1 = R_2 = OH$

D.4.5 (3-Acenaphthyl) hydroquinone succin-as-ein :
$R_2 = R_3 = R_5 = H$; $R_1 = R_4 = OH$

D.4.6 (3-Acenaphthyl) pyrogallol succin-as-ein :
$R_4 = R_5 = H$; $R_1 = R_2 = R_3 = OH$

D.4.7 (3-Acenaphthyl) phloroglucinol succin-as-ein :

$R_2 = R_4 = H; R_1 = R_3 = R_5 = OH$

D.4.8 (3-Acenaphthyl) deacetyl resorcinol succin-as-ein :
$R_2 = R_4 = R_5 = H; R_1 = R_3 = OCOCH_3$

D.4.9 (3-Acenaphthyl) dibromo resorcinol succin-as-ein :
$R_5 = H; R_2 = R_4 = Br; R_1 = R_3 = OH$

D.4.2 (3-ACENAPHTHYL) PHENOL SUCCIN-AS-EIN :

The dye was prepared by condensing the acid (1.5g) and phenol (1.2g) in presence of 5-6 drops of concentrated sulphuric acid. The heating was carried out for six hours at 150-170^{0}C, till brittle mass on cooling was obtained. Excess of phenol was removed by steam distillation. The isolation and purification of the dye were done in the same manner as described in case of other phenol dyes. The purity of the dye was done by paper chromatography.

The green coloured dye has, m.p. 114-116^{0}C. Its ethanolic solution is light yellow in colour, which turns into pink on adding a drop of alkali. With strong alkali it gives pinkish red colour.

Anal. For. : $C_{22}H_{18}O_3$ (mol. wt. 330)

Cala. : C, 80.00; H, 5.45;

Found : C, 79.96; H, 5.43;

D.4.3 (3-ACENAPHTHYL) RESORCINOL SUCCIN-AS-EIN :

The dye was prepared by condensing the acid (3.0g) and resorcinol (2.5g) by using 6-8 drops of concentrated sulphuric acid as condensing agent. Heating was continued for four hours at 120-140^{0}C, till brittle mass was obtained on cooling. The isolation and purification of the dye were done in the same manner as in the case of A 4.3 chapter III, yield 2.6g.

The micro crystalline dye, red in colour has 298-300^{0}C. Its ethanolic solution is yellow in colour which turns into yellowish orange with green flurescence on addition of a drop of alkali. In strong basic medium it gives yellowish orange colour with intense green fluorescence.

Anal. For. : $C_{22}H_{18}O_4$ (mol. wt. 346)

Cala. : C, 76.30; H, 3.76;

Found : C, 76.26; H, 3.75;

D.4.4 (3-ACENAPHTHYL) CATECHOL SUCCIN-AS-EIN:

The dye was prepared isolated &purified in the same manner as described in the case of A.4.3. Chapter III by condensing the acid (1.5g) and catechol (1.5g) at a temperature 130-140^{0}C, yield 0.8g.

The dye is dark brown in colour, m.p. 300^{0}C. Its ethanolic solution is brown in colour which turns into bluish green on addition of alkali.

Anal. For. : $C_{22}H_{18}O_4$ (mol. wt. 346)

Cala. : C, 76.30; H, 5.20;

Found : C, 76.26; H, 5.18;

D.4.5. (3-ACENAPTHYL) HYDROQUINONE SUCCIN-AS-EIN:

Condensation of the acid (1.5g) and hydroquinone (1.5g) was carried out at 170-180^{0}C for four hours by using concentrated sulphuric acid 6-8 drops as condensing agent. Isolation and purification of the dye were done in a similar manner as described in the case of A.4.3 chapter III, yield 60%.

The dark brown dye has m.p. 202-204^{0}C.Its ethanolic solution is reddish brown in colour which turns into purple on addition of alkali.

Anal. For. : $C_{22}H_{18}O_4$ (mol. wt. 346)

Cala. : C, 76.30; H, 5.20;

Found : C, 76.26; H, 5.17;

D.4.6 (3-ACENAPHTHYL) PYROGALLOL SUCCIN-AS-EIN:

The dye was prepared by condensing the acid (1.0g) and pyrogallol (1.2g) in an oil bath at a temperature 160-170^{0}C for about five hours in presence of concentrated sulphuric acid (6-8 drops) as condensing agent. The dye was isolated and purified as the dye A.4.3 chapter III.

The shinning, microcrystalline black dye has m.p. 204-206°C. Its ethanolic solution is light brown which becomes violet on adding a drop of alkali. In strong basic medium it shows blue-black colour.

Anal. For. : $C_{22}H_{18}O_5$ (mol. wt. 362)

Cala. : C, 72.93; H, 3.59;

Found : C, 72.88; H, 3.56;

D.4.7. (3-ACENAPHTHYL) PHLOROGLUCINOL SUCCIN-AS-EIN:

The acid (1.5g) and phloroglucinol (1.5g) were condensed by heating the mixture at180-200^{0}C, for about three and half hours in an oil bath in presence of concentrated sulphuric acid (4-6 drops). The dye was isolated and purified as the dye A.4.3 chapter III, yield 1.2g.

The light brown coloured dye has m.p. 240^{0}C (decomp). It gives light brown colour with ethanol which becomes dark brown on adding a drop of alkali. In strong basic medium it gives dark brown colour.

Anal. For. : $C_{22}H_{18}O_5$ (mol. wt. 362)

Cala. : C, 72.93; H, 4.97;

Found : C, 72.88; H, 4.94;

D.4.8 ACETYLATION OF (3-ACENAPHTHYL) RESORCINOL SUCCIN-AS-EIN:

(3-Acenaphthyl diacetyl resorcinol succin-as-ein)

The dye 3-acenaphthyl resorcinol succin-as-ein was acetylated in the same way as described in the case of acetylation of A.4.8 chapter III. The crude yellow product was treated with animal charcoal and crystallised from aqueous ethanol in presence of 4-5 drops of acetic acid, yield 60%.

The acetylated yellowish white, amorphous derivative has m.p. 140-142^{0}C. It is soluble in ethanol, acetone and acetic acid.

Anal. For. : $C_{22}H_{16}O_4(COCH_3)_2$ (mol. wt. 362)

Cala. : C, 61.39; H, 3.72; Acetyl, 20.00;

Found : C, 61.31; H, 3.70; Acetyl, 19.97;

D.4.9. BROMINATION OF 3-ACENAPHTHYL RESORCINOL SUCCIN-AS-EIN:

(3-Acenaphthyl dibromo resorcinol succin-as-ein)

The dibromo derivative of the dye (3-acenaphthyl resorcinol succin-as-ein) was prepared, purified and crystallised in a similar manner as described in the case of A.4.9 chapter III, yield 60%.

The red microcrystalline dye has m.p. 130-132^{0}C. Its ethanolic solution is yellow in colour, which turns into yellowish orange with green fluorescence on adding a drop of alkali. In strong basic medium it gives deep red colour.

Anal. For. : $C_{22}H_{16}O_4Br_2$ (mol. wt.504)

Cala. : Br, 31.75;

Found : Br, 31.71;

D.4.10 CAUSTIC POTASH TREATMENT OF (3-ACENAPHTHYL) RESORCINOL SUCCIN-AS-EIN:

Caustic potash treatment of the dye was done as A.4.10 chapter III. The following three residues were obtained.

Residue (I):

It was identified to be the unreacted residual dye from its colour reactions and confirmed by mixed melting point determination.

Residue (II):

The yellowish white compound, m.p 216-218^{0}C, gave the usual test of a carboxyl group and was identification as β-(3-acenaphthoyl) propinoic acid and was confirmed by mixed point determination and superimposition of IR spectra with authentic sample.

Residue (III):

The brownish red residue was purified and was identified to be resorcinol from its colour reactions and confirmed by mixed melting point determination with authentic sample.

Bromination , acetylation and caustic potash fusion of the dye was shown in Chart H chapter II.

APPENDIX

APPENDIX

MELTING POINTS, SHADES, COLOURS IN DIFFERENT MEDIA AND ABSORPTION MAXIMA OF THE DYES OBTAINED FROM DIFFERENT ACIDS DESCRIBED IN THE THESIS ARE SUMMARISED BELOW IN TABULAR FORM

(A) λ_{max} of phenolphthalein 550 nm (alkaline medium); fluorencein 460 nm (neutral medium), 500 nm (alkaline) medium; Eosin 530 nm (neutral and alkaline medium were determined).

(B) λ_{max} of phthal-as-eins of tetrachlorophthalic anhydride

Phenolphthalein analogue 585 nm (alkaline medium); Fluorescien analogue 470 nm and 500 nm (neutral medium), 520 nm (alkaline medium); Eosin analogue 520 nm and 560 nm (neutral medium). 550 nm (alkaline medium) were determined.

(C) λ_{max} of phthal-as-eins of 3-nitro phthalic anhydride

Phenolphthalein analogue 560 nm (alkaline medium); Fluorescein analogue 480 nm (neutral medium), 510 nm (alkaline medium); Eosin analogue 530 nm (neutral medium), 540 nm (alkaline medium) were determined.

(D) λ_{max} of succin-as-eins

Fluorescein analogue 480-485 nm (neutral medium), 490-500 nm (alkaline medium) were determined.

DYES DERIVED FROM 2-(2',4' DIMETHYL BENZOYL) BENZOIC ACID :

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	brown -	178-180^{0}C -	light yellow	pink -	pink -	520 530	6.5 9.6	neutral alkaline
Resorcinol	orange yellow -	156-158^{0}C - -	yellow - -	brownish yellow G. F.	reddish brown G. F.	460 490 -	6.4 9.8 -	neutral alkaline -
Catechol	black -	>360^{0}C -	brown -	brown -	black -	- -	- -	neutral alkaline
Hydroquinone	black -	>360^{0}C -	golden yellow	brown -	dark brown	- -	- -	neutral alkaline
Pyrogallol	black -	>360^{0}C -	wine red	wine red	violet -	- -	- -	neutral alkaline
Phloroglucinol	dark brown	>360^{0}C	dark brown	lemon yellow	orange -	- 490	- 8.4	neutral alkaline
Diacetyl compound	light yellow	110-112^{0}C -	colour less	yellowish G. F.	yellowish G. F.	- -	- -	neutral alkaline
Dibromo copound	dirty orange -	90-91^{0}C -	yellowish red -	yellowish orange G. F.	deep red -	530 530 -	6 9 -	neutral alkaline

DYES DERIVED FROM 2-(3'-CARBMETHOXY-4'-HYDROXY BENZOYL) BENZOIC ACID :

Phenols	Shade of dye	m.p. ^{0}C	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	orange	126-127^{0}C	light	red	pink	455	6.8	neutral
	-	-	brownish	-	-	495	9.5	alkaline
Resorcinol	red	183-185^{0}C	golden	reddish	reddish	520	6.7	neutral
	-	-	-	yellow	brown	560	9.6	alkaline
	-	-	-	G. F.	G. F.	-	-	-
Catechol	black	>300^{0}C	slightly	brown	brown	-	-	neutral
	-	-	brown	colour	colour	-	-	alkaline
Hydroquinone	black	>300^{0}C	crimson	dark	dark	-	-	neutral
	-	-	colour	brown	brown	-	-	alkaline
Pyrogallol	black	>360^{0}C	wine	violet	violet	-	-	neutral
	-	-	red	-	-	-	-	alkaline
Phloroglucinol	dark	>360^{0}C	golden	reddish	reddish	-	-	neutral
	orange	-	yellow	orange	orange	-	-	alkaline
Diacetyl compound	light	200-202^{0}C	light	bright	bright	-	-	neutral
	yellow		yellow	yellow	yellow	-	-	alkaline
	-	-	G.F.	G. F.	G. F.	-	-	-
Dibromo copound	pale	256-257^{0}C	orange	yellowish	yellowish	450	6.6	neutral
	orange	-	-	pink	pink	480	9.6	alkaline
	-	-	-	G. F.	G. F.	-	-	-

DYES DERIVED FROM 2-(5' CHLORO 2' CHLOROMETHYL BENZOYL) BENZOIC ACID :

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol		Colour with 2% NaOH	λ_{max} nm	pH	Medium
			Neutral	Alkaline				
Phenol	dark	118-119^{0}C	reddish	pink	pink	520	9.4	neutral
	brown		green	-	-	450	6.2	alkaline
Resorcinol	red	268-269^{0}C	golden	reddish	reddish	480	9.6	neutral
	-	-	yellow	yellow	yellow	-	-	alkaline
	-	-	-	G. F.	G. F.	-	-	-
Catechol	black	>360^{0}C	brownish	black	black	-	-	neutral
	-	-	black	-	-	-	-	alkaline
Hydroquinone	black	>360^{0}C	brown	blackish	blackish	-	-	neutral
	-	-	-	brown	brown	-	-	alkaline
Pyrogallol	black	>360^{0}C	brown	blackish	blackish	-	-	neutral
	-	-	-	brown	brown	-	-	alkaline
Phloroglucinol	reddish	180^{0}C	golden	dark	dark	-	-	neutral
	brown	-	yellow	reddish	reddish	480	8.6	alkaline
Diacetyl compound	pale	184-186^{0}C	allmost	yellowish	yellowish	-	-	neutral
	yellow	-	colour less	G. F.	G. F.	-	-	alkaline
Dibromo copound	dark	294-296^{0}C	yellow	yellowish	yellowish	525	6.2	neutral
	orange	-	-	G. F.	G. F.	535	9	alkaline

DYES DERIVED FROM (3'-ACENAPHTHOYL) BENZOIC ACID :

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol: Neutral	Colour in ethanol: Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	grey	$110-112^0C$	light	pink	pinkish	500	6.3	neutral
	-	-	yellow	-	red	530	8.8	alkaline
Resorcinol	red	$309-311^0C$	yellow	yellowish	yellowish	455	5.8	neutral
	-	-	-	orange	orange	500	9	alkaline
	-	-	-	with G.F	with G.F	-	-	-
Catechol	dark	$>360^0C$	brown	bluish	bluish	-	-	neutral
	brown	-	-	Green	Green	-	-	alkaline
Hydroquinone	dark	$>360^0C$	reddish	purple	purple	-	-	neutral
	brown	-	brown	-	-	-	-	alkaline
Pyrogallol	black	$205-260^0C$	reddish	violet	blue	-	-	neutral
	-	-	brown	-	black	-	-	alkaline
Phloroglucinol	light	245^0C	light	dark	dark	-	-	neutral
	brown	-	brown	brown	brown	500	8.6	alkaline
Diacetyl compound	yellowish	$146-148^0C$	light	yellowish	yellowish	530	5.5	neutral
	white	-	yellow	G. F.	G. F.	530	9.5	alkaline
Dibromo copound	brick	$134-136^0C$	yellow	yellowish	deep	-	-	neutral
	red	-	-	orange	red	-	-	alkaline

DYES DERIVED FROM 2-(2' 4' DIMETHYL BENZOYL) TETRA CHLORO BENZOIC ACID :

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	pink	230-232^{0}C	wine	violet	violet	530	6.8	neutral
	-	-	reddish	-	-	560	9.5	alkaline
Resorcinol	golden	280-282^{0}C	creman	pink	pink	510	6.5	neutral
	brown	-	colour	orange	orange	530	9.6	alkaline
	-	-	-	with G.F	with G.F	-	-	-
Catechol	black	248-250 ^{0}C	brown	brown	brown	-	-	neutral
	-	-	-	-	-	-	-	alkaline
Hydroquinone	light	>320^{0}C	golden	golden	dark	-	-	neutral
	black	-	brown	brown	brown	-	-	alkaline
Pyrogallol	blackish	>360^{0}C	golden	brown	dark	-	-	neutral
	brown	-	brown	-	brown	-	-	alkaline
Phloroglucinol	dark	248^{0}C	dark	dark	dark	-	-	neutral
	orange	-	red	red	red	-	-	alkaline
Diacetyl compound	buff	314-316^{0}C	light	pink	pink	-	-	neutral
	-	-	brown	G. F.	G. F.	-	-	alkaline
Dibromo copound	pale	119-120^{0}C	yellowish	pink	pink	440	6.6	neutral
	yellow	-	pink	-	-	460	9.5	alkaline

DYES DERIVED FROM 2-(3'-CARBMETHOXY 4'-HYDROXY BENZOYL) TETRA CHLORO BENZOIC ACID

Phenol	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	orange	240-242^{0}C	golden	violet	violet	460	6.8	neutral
	-	-	yellow	-	-	500	9.2	alkaline
Resorcinol	light	280-282^{0}C	pale	reddish	reddish	510	6.5	neutral
	brown	-	yellow	orange	orange	530	9.5	alkaline
	-	-	-	G. F.	G. F.	-	-	-
Catechol	light	120-130^{0}C	light	blackish	blackish	-	-	neutral
	black	-	black	brown	brown	-	-	alkaline
Hydroquinone	black	300^{0}C	light	light	light	-	-	neutral
	-	-	brown	brown	brown	-	-	alkaline
Pyrogallol	brown	>360^{0}C	wine	blue	blue	-	-	neutral
	-	-	red	-	-	-	-	alkaline
Phloroglucinol	dark	> 300^{0}C	wine	red G.F	red G.F	-	-	neutral
	orange	-	red	-	-	-	-	alkaline
Diacetyl compound	golden	166-168^{0}C	light	pink	pink	-	-	neutral
	brown	-	pink	G. F.	G. F.	-	-	alkaline
Dibromo copound	pale	308-309^{0}C	pinkish	dark	dark	440	6.5	neutral
	yellow	-	orange	pink	pink	460	9.5	alkaline
	-	-	-	G. F.	G. F.	-	-	-

DYES DERIVED FROM 2-(5'-CHLORO 2'-CHLOROMETHYL BENZOYL) TETRA CHLORO BENZOIC ACID

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol: Neutral	Colour in ethanol: Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	pink	248-250^{0}C	light	rose	rose	510	5.9	neutral
	white		yellow	red	red	530	9	alkaline
Resorcinol	golden	296-298^{0}C	deep	pink	pink	455	5.6	neutral
	yellow	-	orange	G. F.	G. F.	500	9.5	alkaline
	-	-	G. F.	-	-	-	-	-
Catechol	black	256-258^{0}C	light	dark	dark	-	-	neutral
	-	-	brown	brown	brown	-	-	alkaline
Hydroquinone	blackish	>300^{0}C	leaf	brown	brown	-	-	neutral
	brown	-	brown	-	-	-	-	alkaline
Pyrogallol	blackish	>360^{0}C	leaf	violet	violet	-	-	neutral
	brown	-	brown	-	-	-	-	alkaline
Phloroglucinol	blackish	320^{0}C	golden	dark	dark	-	-	neutral
	brown	-	brown	red	red	490	8.5	alkaline
Diacetyl compound	buff	160-162^{0}C	light	pink	pink	-	-	neutral
	-	-	yellow	-	-	-	-	alkaline
Dibromo copound	blackish	326-328^{0}C	pinkish	pink	pink	520	5.5	neutral
	rose	-	G. F.	G. F.	G. F.	530	10	alkaline

DYES DERIVED FROM 2-(3'-ACENAPHTHOYL) TETRA CHLORO BENZOIC ACID :

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	brown	249-251^0C	light brown	pink	pink	510	6.2	neutral
	-	-		-	-	530	9.4	alkaline
Resorcinol	reddish brown	291-293^0C	yellow	yellowish G. F.	yellowish G. F.	470	5.8	neutral
		-	-			510	8.7	alkaline
	-	-	-	-	-	-	-	-
Catechol	black	260^0C	blalish green	blackish green	blackish green			neutral
	-	-				-	-	alkaline
Hydroquinone	reddish black	144-146^0C	red	deep red	deep red	-	-	neutral
		-	-			-	-	alkaline
Pyrogallol	dark brown	>300^0C	brown	violet	violet	-	-	neutral
		-	-	-	-	-	-	alkaline
Phloroglucinol	dark brown	>300^0C	light brown	deep brown	deep brown	-	-	neutral
		-				490	9.5	alkaline
Diacetyl compound	light yellow	245-247^0C	pink	pinkish G. F.	pinkish G. F.	-	-	neutral
		-	-			-	-	alkaline
Dibromo copound	black red	165^0C	yellowish orange	reddish orange G. F.	deep red	510	6.3	neutral
		-				520	9.8	alkaline
	-	-	-		-	-	-	-

DYES DERIVED FROM 2-(2' 4' DIMETHYL BENZOYL)-3-NITRO BENZOIC ACID :

Phenol	Shade of dye	m.p. ^0C	Colour in ethanol		Colour with 2% NaOH	λ_{max} nm	pH	Medium
			Neutral	Alkaline				
Phenol	brown	177-118^{0}C	light	light	violet	510	6.2	neutral
	-	-	yellow	violet	-	530	9.5	alkaline
Resorcinol	brown	284-286^{0}C	brown	brownish	reddish	520	6.5	neutral
	-	-	-	red	brown	540	9.6	alkaline
	-	-	-	G. F.	G. F.	-	-	-
Catechol	black	360^{0}C	brown	blackish	blackish	-	-	neutral
	-	-	-	brown	brown	-	-	alkaline
Hydroquinone	black	210^{0}C	light	dark	dark	-	-	neutral
	-	-	brown	brown	brown	-	-	alkaline
Pyrogallol	black	>360^{0}C	light	violet	violet	-	-	neutral
			brown			-	-	alkaline
Phloroglucinol	brownish	340^{0}C	brown	red	red	-	-	neutral
	red	-	-	-	-	-	-	alkaline
Diacetyl compound	yellow	235-236^{0}C	brown	reddish	reddish	-	-	neutral
	-	-	-	brown	brown	-	-	alkaline
Dibromo copound	dirty	212^{0}C	wine	red	red	520	6.5	neutral
	orange	-	red	G. F.	G. F.	545	9.8	alkaline

DYES DERIVED FROM 2-(3' CARBMETHOXY 4' HYDROXY BENZOYL) BENZOIC ACID :

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	orange	135-136^{0}C	brownish	pink	pink	460	6.5	neutral
	-	-	red	-	-	500	9.5	alkaline
Resorcinol	red	190-192^{0}C	yellowish	yellowish	reddish	520	6.5	neutral
	-	-	red	orange	brown	560	9.6	alkaline
	-	-	G. F.	G. F.	G. F.	-	-	-
Catechol	black	>360^{0}C	brown	bownish	bownish	-	-	neutral
	-	-	-	black	black	-	-	alkaline
Hydroquinone	black	>300^{0}C	light	brown	brown	-	-	neutral
	-	-	brown	-	-	-	-	alkaline
Pyrogallol	black	>340^{0}C	light	violet	violet	-	-	neutral
	-	-	red	-	-	-	-	alkaline
Phloroglucinol	yellowish	>340^{0}C	golden	reddish	reddish	-	-	neutral
	orange	-	yellow	orange	orange	-	-	alkaline
Diacetyl compound	light	210-212^{0}C	light	brigt	brigt	-	-	neutral
	yellow		yellow G.F.	yellow	yellow	-	-	alkaline
Dibromo copound	pale	248-250^{0}C	yellowish	orange	orange	450	6.5	neutral
	orange	-	orange	G. F.	G. F.	480	9.6	alkaline

DYES DERIVED FROM 2-(5'-CHLORO 2'CHLORO METHYL BENZOYL)3-NITRO BENZOIC ACID :

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	light	222-224^{0}C	light	violet	violet	-	-	neutral
	pink	-	brown	-	-	530	9.5	alkaline
Resorcinol	golden	225-227^{0}C	brown	reddish	reddish	450	5.7	neutral
	yellowish	-	-	brown	brown	520	8.5	alkaline
	-	-	-	-	-	-	-	-
Catechol	black	315-317^{0}C	brown	reddish	reddish	-	-	neutral
	-	-	-	brown	brown	-	-	alkaline
Hydroquinone	blackish	320-321^{0}C	brown	reddish	reddish	-	-	neutral
	brown	-	-	brown	brown	-	-	alkaline
Pyrogallol	black	340-342^{0}C	reddish	dark	dark	-	-	neutral
	-	-	brown	brown	brown	-	-	alkaline
Phloroglucinol	brown	292-294^{0}C	wine	dark	wine	-	-	neutral
	-	-	red	red	red	510	9.1	alkaline
Diacetyl compound	buff	272-274^{0}C	almost	pink	pink	-	-	neutral
	-	-	colourless	-	-	-	-	alkaline
Dibromo copound	yellowish	278-280^{0}C	yellowish	orange	deep	530	6.5	neutral
	orange	-	red	G. F.	red	530	8.8	alkaline

DYES DERIVED FROM 2-(3' ACENAPHTHOYL) 3-NITRO BENZOIC ACID :

Phenols	Shade of dye	m.p. °C	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	grey	115-117°C	light	pink	pinkish	500	6.1	neutral
	-	-	yellow		red	520	8.6	alkaline
Resorcinol	red	315-317°C	yellow	yellowish	yellowish	450	5.6	neutral
	-	-	-	orange	orange	510	8.9	alkaline
	-	-	-	G. F.	G.F	-	-	-
Catechol	dark	>300°C	brown	bluish	bluish	-	-	neutral
	brown			green	green	-	-	alkaline
Hydroquinone	dark	202-204°C	brownish	purple	purple	-	-	neutral
	brown	-	red	-	-	-	-	alkaline
Pyrogallol	black	215-217°C	reddish	violet	blue	-	-	neutral
	-	-	brown	-	black	-	-	alkaline
Phloroglucinol	light	240°C	light	dark	dark	480	10	neutral
	brown	-	brown	brown	brown	-	-	alkaline
Diacetyl compound	yellowish	146-148°C	colour	yellowish	yellowish	-	-	neutral
	white		less	G. F.	G.F	-	-	alkaline
Dibromo copound	brick	130-132°C	yellow	yellowish	deep	520	6	neutral
	red	-	-	orange	red	530	9.2	alkaline

DYE DERIVED FROM β-(2,4-DIMETHYL BENZOYL) PROPIONIC ACID

Phenol	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	dark brown	148-149^{0}C	yellow	brown	brown	500	5.9	neutral
	-	-	-	-	-	540	9.5	alkaline
Resorcinol	yellowish brown	220-222^{0}C	golden yellow	wine red	wine red	460	6.5	neutral
	-	-				500	9.6	alkaline
	-	-	-	G. F.	G. F.	-	-	-
Catechol	black	>360^{0}C	light brown	dark brown	dark brown	-	-	neutral
	-	-				-	-	alkaline
Hydroquinone	black	240^{0}C	light brown	dark brown	dark brown	-	-	neutral
	-	-				-	-	alkaline
Pyrogallol	black	>360^{0}C	crimson	dark red	dark red	-	-	neutral
	-	-	-			-	-	alkaline
Phloroglucinol	dark brown	180^{0}C	light brown	brown	dark brown	-	-	neutral
						500	8.6	alkaline
Diacetyl compound	brown	320-322^{0}C	light brown	yellowish G. F.	yellowish G. F.	-	-	neutral
	-	-				-	-	alkaline
Dibromo copound	dark brown	150-151^{0}C	yellow red	yellow orange	deep red	520	6.4	neutral
		-				530	9.5	alkaline
	-	-	-	G. F.	G. F.	-	-	-

DYE DERIVED FROM β-(3-CARBMETHOXY-4-HYDROXY BENZOYL) PROPIONIC ACID

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	blackish brown	$102-103^0C$	yellowish brown	pinkish red	pinkish red	510	5.6	neutral
		-				520	8.6	alkaline
Resorcinol	reddish orange	$86-88^0C$	light red	yellowish orange	orange	455	6.2	neutral
		-			-	500	9.8	alkaline
	-	-	-	G. F.	-	-	-	-
Catechol	dark brown	$116-118^0C$	brown	brown	black	-	-	neutral
		-	-	-	-	-	-	alkaline
Hydroquinone	black	$242-244^0C$	light brown	brownish red	brownish red	-	-	neutral
	-	-				-	-	alkaline
Pyrogallol	black	$>360^0C$	blackish brown	black	black	-	-	neutral
	-	-		-	-	-	-	alkaline
Phloroglucinol	yellowish red	300^0C	reddish brown	red	red	510	8.6	neutral
		-		-	-	-	-	alkaline
Diacetyl compound	brown	$82-84^0C$	light yellow	brown	brown	-	-	neutral
	-	-		-	-	-	-	alkaline
Dibromo copound	brown	$>360^0C$	yellowish red	violet	voilet	520	6.2	neutral
	-	-		-	-	530	9.8	alkaline

DYE DERIVED FROM β (5 CHLORO 2 CHLOROMETHYL BENZOYL) PROPIONIC ACID

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	blackish brown	101-103^{0}C	yellowish brown	pinkish red	pinkish red	520	5.9	neutral
		-				530	9.2	alkaline
Resorcinol	reddish orange	86-88^{0}C	light red	yellowish orange	orange	460	5.6	neutral
	-	-			-	510	9.5	alkaline
		-	-	G. F.	-	,	,	-
Catechol	brown	116-118^{0}C	brown	black	black	,	,	neutral
	-	-	-	-	-	,	,	alkaline
Hydroquinone	black	260-262^{0}C	light brown	brownish red	brownish red	,	,	neutral
	-	-				,	,	alkaline
Pyrogallol	black	>360^{0}C	blackish brown	black	black	,	,	neutral
	-	-		-	-	,	,	alkaline
Phloroglucinol	yellowish red	300^{0}C	reddish brown	red	red	490	8.6	neutral
		-		-	-	,	,	alkaline
Diacetyl compound	brown	78-80^{0}C	light yellow	brown	brown	,	,	neutral
	-	-		-	-	,	,	alkaline
Dibromo copound	brown	>360^{0}C	yellowish red	violet	violet	520	5.5	neutral
	-	-		-	-	530	9.2	alkaline

DYE DERIVED FROM β-(3-ACENAPHTHOYL)PROPIONIC ACID

Phenols	Shade of dye	m.p. ^0C	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ_{max} nm	pH	Medium
Phenol	green -	114-116^{0}C -	light yellow	pink -	pinkish red	510 530	6.3 8.8	neutral alkaline
Resorcinol	red - -	298-300^{0}C - -	yellow - -	yellowish orange G. F.	yellowish orange G. F.	460 510 -	5.8 8.6 -	neutral alkaline -
Catechol	dark brown	300^{0}C	brown	bluish green	bluish green	- -	- -	neutral alkaline
Hydroquinone	dark brown	202-204^{0}C -	reddish brown	purple -	purple -	- -	- -	neutral alkaline
Pyrogallol	black -	204-206^{0}C -	light brown	violet	blue black	- -	- -	neutral alkaline
Phloroglucinol	light brown	240^{0}C	light brown	dark brown	dark brown	- 500	- 8.4	neutral alkaline
Diacetyl compound	yellowish white	140-142^{0}C -	light yellow	yellowish G. F.	yellowish G. F.	- -	- -	neutral alkaline
Dibromo copound	red - -	130-132^{0}C - -	yellow - -	yellowish orange G. F.	deep red -	520 530 -	6.3 9.8 -	neutral alkaline -